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POLYMERIZATION FILM-FORMING MATERIALS

by

V. I. Yeliseyev

COUNTRY: USSR

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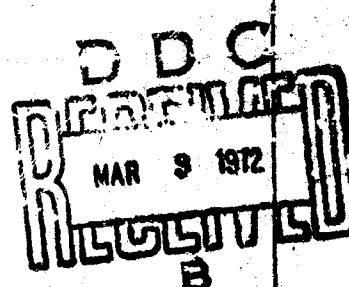
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13. ABSTRACT

This book describes methods of production and properties of polymerization film formers, as well as methods of production of coatings based on them. It consists of two sections: the first section discusses problems of the mechanism of production of polymerization film formers and the formation of coatings as well as the aging of polymers and their resistance to various corrosive media; the second section presents the characteristics of monomers, the properties of paint and varnish materials and coatings.

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FOREWORD

The production of paint and varnish materials is developing rapidly, together with the development of the chemistry and technology of polymers. In the technically developed countries, the production of plastics amounts to between 15 and 28 kg per unit of population; the production of paint and varnish materials based on synthetic film formers (resins) and vegetable oils is from 10 to 17 kg per unit of population.

Analysis of the contemporary state of the production of paint and varnish materials in the USSR and abroad indicates that during the post-war period, various synthetic film formers have begun replacing vegetable oils on an increasing scale.

In spite of the predominance of condensation resins in the total volume of synthetic film-forming materials, the significance of polymerization resins has continued to increase. An illustrative example is the USA, where 33.4% of the world's production of paint and varnish materials occurs; almost half of the acrylic and about 20% of the methacrylic polymers produced there are consumed by the paint and varnish industry. Beginning in 1964, the automobile industry -- the largest single consumer of this type of product -- went over almost completely to the use of acrylic resins. Intensive developments in this area are also being conducted in Japan, West Germany and other countries.

The reason for this is that the use of polymerization film formers opens new possibilities for the production of high qua..ty coatings. The introduction of various functional groups to the composition of a resin by copolymerization of the corresponding monomers allows the mechanical properties and adhesion of coatings to be changed, increasing their corrosion and biological resistance, producing coatings with a reticular structure. One new and particularly interesting method for the production of coatings in a thin

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layer directly of monomers without solvents is based exclusively on polymerization processes.

Copolymerization of ordinary monomers with monomers containing ionizing groups is used to produce water-soluble film formers which can be applied by electrodeposition.

In the Soviet Union, which occupies second place in the world as to the volume of production of paint and varnish materials, the type of polymerization film formers produced in the greatest volume is latex. Although the share of these materials produced is not as yet great, work has been intensified in recent years on their creation and introduction to production. Latex paint and varnish materials are widely used in construction, where they are replacing materials based on vegetable oils.

Studies performed in the area of emulsion polymerization and the mechanism of formation of coatings are providing new capabilities for modification and improvement of latex film formers. One of the most interesting prospects for utilization of materials based on latex is the production of reticular-structure coatings, particularly those which cure at room temperature.

This monograph is designed to reveal the present level and prospects for development of science and production in the area of the synthesis and properties of polymerization film formers, as well as processes of production of coatings from them. The book presents detailed analysis of problems concerning the most promising methods of production of polymerization film formers -- latex polymerization and thin layer polymerization. The traditional method of production of paint -- by polymerization in organic solvents -- is discussed in less detail, since it has been described in a number of special monographs.

This book presents a systematic review of works performed in the area of latex polymerization both in the USSR and abroad. The following are discussed in greatest detail: the influence of the method of performance of latex polymerization on the properties of the latex, the relationship between the solubility of monomers in water and the kinetics of polymerization, the development of supermolecular structures during the process of polymerization and the dependence of properties of the coatings formed on these structures, the influence of the chemical composition of the polymer (presence of functional groups) on the mechanism of formation of coatings of latexes. The stability of latex systems, which is particularly important for these film formers, is studied separately.

In addition to these problems, the book presents the properties of monomers used for the production of film forming materials based on latex, varnish and water-soluble film formers. Significant space is given to analysis of modifying monomers, the use of which allows the quality and operational properties of coatings, particularly latex coatings, to be improved. One chapter is dedicated to the aging of polymers and their resistance to various corrosive media.

The work on this book involves the participation of a group of workers at the laboratory of synthesis of film-forming agents of the Institute of Physical Chemistry, Academy of Sciences, USSR: I. S. Avetisyan, T. V. Bakayeva, V. D. Gerber, V. I. Yeliseyeva, N. G. Zharkova, L. V. Kozlov, Ye. M. Morozova, I. V. Nazarova and I. S. Pinskaya.

This monograph is the first attempt at systematization of material on the synthesis of polymerization film formers and the properties of paint and varnish materials based on them. The authors will be grateful to any readers who will send in critical comments.

SECTION I

MECHANISM OF PRODUCTION OF POLYMERIZATION
FILM-FORMING MATERIALS, FORMATION AND AGING
OF COATINGS BASED ON THEM

Polymerization film formers are produced by radical polymerization and monomers. The most common industrial method is emulsion (latex) polymerization, which occurs very rapidly at relatively low temperatures. Under these conditions, polymers can be produced with high molecular weight and narrow molecular weight distribution. When polymerization is performed in aqueous phase, the heat of the reaction is easily carried away and the necessity of using toxic and expensive solvents is eliminated.

The attention of paint and varnish workers has been attracted by a new method of production of coatings -- polymerization of monomers directly on the substrate without organic solvents, which simplifies the process and makes it economically desirable.

In addition to these methods, polymerization is frequently performed in an organic solvent, which method has been rather well studied and described. This method is used to produce varnish film formers (polymer solutions in organic solvents) and water-soluble film formers (polymer solutions in dilute alkalis).

CHAPTER I

LATEX FILM FORMERS

Polymerization Mechanism

Latex polymerization is performed in aqueous phase in the presence of emulsifiers -- surface-active agents such as soap or oxyethylated products. Water-soluble or oil-soluble initiators are used.

The properties of latexes depend not only on the composition and mode of their production, but to a significant extent on the method of performance of the process. Until recent years, the periodic (1-stage) method was most frequently used, in which all the reacting components were placed in the reactor simultaneously. At the present time, continuous and semi-continuous methods are becoming popular, in which the reacting components are added as the reaction occurs. The periodic method has been most fully studied [1-20]. Since the process occurs in the presence of the monomer emulsion, it has come to be called emulsion polymerization, although actually the polymerization occurs in smaller particles than the droplets of the monomer emulsion, and the process should more properly be called latex polymerization.

Until recently, the physical and chemical regularities of emulsion polymerization were studied primarily on the basis of systems imitating the periodic method of production of latexes, primarily on the basis of monomers little soluble in water. Subsequently, works have been performed on the processes of polymerization of monomers which are significantly soluble in water, polymerization without introduction of an emulsifier, polymerization with various concentrations with monomers in the system, as well as electron microscope studies of the fine structure of the latex particles. These studies have produced new information on emulsion polymerization, in particular on the kinetics of the process, the colloidal stability of the systems, structural pecularities of the polymers being formed, and the influence of the aqueous phase and solubility of the initial monomers.

Influence of solubility of monomers in water on polymerization process.

Polymerization of monomers, little soluble in water. Studying polymerization of monomers of this type in the presence of water-soluble initiators, Harkins [4, 5] and Yurzhenko [2, 3] based their studies on the assumption that the process occurs in a colloidal solution of emulsifier in the micelles, capable of dissolving the monomer in their internal (hydrophobic) portion. The contact between the primary radicals formed in the aqueous phase and the monomers is achieved in the micelles, due to which it is in the micelles that polymerization is initiated. The growth of polymer radicals in the micelles occurs due to the monomer contained in them, which is present in dynamic equilibrium with the monomer dissolved in the aqueous phase, where its concentration remains constant as long as monomer droplets are present. Polymerization

occurs in the polymer-monomer particles formed. After the concentration of
emulsifier in the solution falls below the critical concentration of micelle
formation (due to adsorption of the growing particles by its surface), the
number of polymer-monomer particles in the system remains constant and poly-
merization occurs in each particle formed, Harkins [4,5] suggested the follow-
ing diagram for emulsion polymerization (Fig. 1.1).

A mathematical interpretation of the model of emulsion polymerization
suggested by Harkins was presented by Smith and Ewart [12], who produced
equations relating the overall rate of polymerization and the number of poly-
mer-monomer particles formed to the concentration of emulsifier and initiator
in the system. They based their calculations on the fact that polymerization
in latex particles follows the general kinetic regularities of radical poly-
merization in a mass. Deviations occur only as a result of the occurrence
of polymerization not in a single phase, but rather in many discrete particles
-- the micelles of the emulsifier, and then in the polymer-monomer particles.
They assumed that each particle can contain not over one radical over the
course of half of the polymerization time, and that the separation of poly-
mer radicals occurs when the first radical enters the particle from the
aqueous phase. Since the concentration of monomer in the particles is con-
sidered constant, as long as the monomer drops are present, the total rate
of polymerization in this stage is described by the equation

$$v = K \, [I]^{0.4} \, [E]^{0.4} \, [M]^{0} \tag{1}$$

where K is the proportionality factor;
   [I] is the concentration of initiator;
   [E] is the concentration of emulsifier;
   [M] is the concentration of monomer.
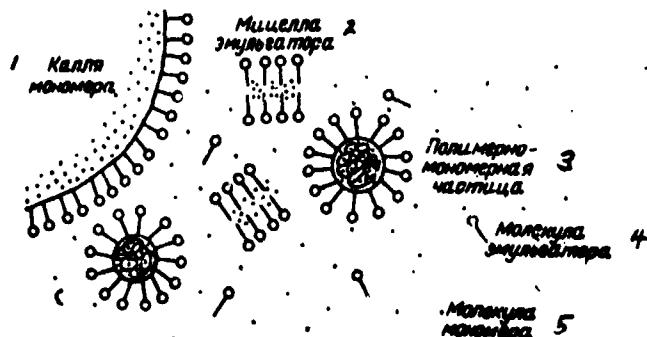
Fig. 1. 1. Diagram of Emulsion Polymerization According to Harkins.
1. Monomer Drop; 2. Emulsifier Micelle; 3. Polymer-monomer
particles; 4. Emulsifier Molecule; 5. Monomer Molecule.

Medvedev [6-8], in studying emulsion polymerization, bases his studies
on the assumption that in the stage of the process when there are emulsifier
micelles with the property of clusters present, exchange of molecules and
radicals occurs between individual micelles, as well as between micelles and
the polymer-monomer particles which form. The presence of this interphase

exchange allows us to look upon the processes occurring involving the micelles as quasihomogeneous with averaging with respect to the concentration of emulsifiers.

Since the rate of polymerization and the mean molecular weight of the polymer do not differ in the stage when emulsifier micelles are present and following its full adsorption by the polymer-monomer particles, the concept of homogeneity can be applied to both stages of the process. Since the viscosity of the polymer-monomer particles increases as the polymer is formed and the penetration of radicals is thereby hindered, the process of latex polymerization occurs in adsorption layers of the emulsifier, and therefore, the volume of adsorption layers of the emulsifier is the basic factor determining the kinetics of the process. The water-soluble initiator can form primary radicals either in the aqueous phase or in the adsorption layers of the emulsifier. An oil-soluble initiator enters the particle together with the monomer. In the former case the free radicals are partially recombined in the aqueous phase, and some of them are captured by the adsorption layers. In both cases, the polymerization process causes free radicals, present in the adsorption layers of the emulsifier. Based on these assumptions, Medevev suggests the following kinetic regularities for the first and second cases of polymerization:

$$v = K [I]^{0.5} [E]^{0.5} [M]^{0} \tag{2}$$
$$v = K [I]^{0.5} [E] [M]^{0} \tag{3}$$

Later, he refines these equations, replacing $[M]^{0}$ with the concentration of monomer in the surface zone.

Although experimental proof of the correctness of equations (1) and (2) is made difficult by the slight difference between them, Brodnyan [15] still considers that equation (2) corresponds more closely to the experimental data. However, he suggests that there is more than one mechanism to the process, considering that the ratio of surface to volume of latex particles changes during the process of polymerization.

Melkonyan[1] develops the concepts of Medevev of the adsorption layer of the emulsifier as the area in which the process primarily occurs. Assuming that the initiator is distributed between the aqueous phase and the adsorption layers of the emulsifier in correspondence to the Langmuir adsorption equation, he suggests the following mechanism for the process: the primary radicals are formed mostly in the adsorption layers of the emulsifier, in which the initiator molecules are polarized; the monomer molecules which enter this zone are also polarized, as a result of which group initiation and group attachment occur during the process of growth. In this case, the adsorption layers of

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[1] Melkonyan, L. G., author's abstract of dissertation, Yerevan State University, 1968.

the emulsifier have an orienting influence on the structure of the polymer formed. Along with the polymerization in the adsorption layers, Melkonyan assumes polymerization to occur in the volume of the polymer-monomer particles during the stage of disappearance of monomer drops from the reaction mass and adsorption of the entire monomer by particles of the polymer.

Considering these assumptions, the author produces an equation for the dependence of the polymerization rate on concentration of emulsifier and initiator, which takes the form of equation (2) for low concentrations of water-soluble initiator.

Polymerization of monomers which are highly soluble in water. In recent times, a number of works have appeared on emulsion polymerization of monomers having significant water solubility [21-32]. These monomers include vinyl acetate, the lower alkyl acrylates and alkyl methacrylates, which are of particular interest for the synthesis of film-forming latexes.

In studies dedicated to the polymerization of these monomers, it has been demonstrated that kinetic equation (1) is not followed, since the number of particles formed depends not only on the concentration of emulsifier, but also on the water solubility of the macroradicals formed [23]. Furthermore, it is assumed that the solubility of the monomer in water, related to a decrease in interphase tension at the boundary between the polymer-monomer particle and the aqueous phase, has a significant influence both on the adsorption of the emulsifier and on the kinetics of polymerization.

In the models and equations suggested for latex polymerization of monomer which are little soluble in water, it is assumed that adsorption of the emulsifier by the surface of the particles formed encounters no difficulties right up to formation of saturated adsorption layers. However, the number of particles formed per unit volume (or the amount of surface formed, which is directly dependent on it) is determined by the concentration of emulsifier, only when the interphase tension is rather high, since according to the equation of Gibbs

$$\Gamma = -\frac{[E]}{RT} \cdot \frac{d\sigma_{1-2}}{d[E]}$$

where Γ is the concentration of adsorbed emulsifier on 1 cm^2 of the polymer surface;
σ_{1-2} is the interphase tension at the boundary between the polymer-monomer particle and the aqueous phase.

The interphase tension is a function of the polarity of the polymer-monomer phase, which depends on the dipole moment and polarization of polar groups of monomer and macrochains. The polarity of the polymer-monomer phase, on the one hand, decreases its adsorption of the emulsifier, while on the other hand it can be an additional stabilization factor. When the polar groups of macrochains are oriented on the surface of the polymer phase, this surface does not

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participate fully in the adsorption of the ionogenic emulsifier. Thus, it has been demonstrated [33] that in the case of polymerization of methylacrylate, initiated by persulfate, in the presence of alkyl sulfonate as an emulsifier, the maximum adsorption of the alkyl sulfonate by the surface of the latex particles is not over 30%. During polymerization of butyl methylacrylate, which is practically insoluble in water, it is 43%. This means that even during polymerization of hydrophobic monomers. some of the surface of the particles formed does not participate in the adsorption of the emulsifier. The same thing is confirmed by the work of Van den Hul and Van der Hoff [34]: polystyrene layers, produced with various emulsifiers, remain stable following complete desorption of the emulsifiers by ion-exchange resins. It is believed that this is facilitated by the presence of a strong acid (SO_4^-) on the surface of the particles of the ionogenic groups, chemically bonded to the macrochains during persulfonate initiation of the polymerization process.

The interphase tension at the boundary of the particle surface with the aqueous phase influences not only the kinetics of formation of particles, but also the rate of polymerization in them. This is related to the fact that even when the monomer is mixed with the polymer in all ratios, its concentration in the particles depends on the interphase tension.

Equilibrium swelling of latex particles in the presence of the free monomers is similar to the equilibrium swelling of a reticular polymer in a solvent [35]. The force limiting swelling in latex particles is not the intermolecular bonds, as in reticular polymers but rather the surface energy at the boundary between the particle surface and the aqueous phase. Consequently, if a swollen particle is in equilibrium with the free monomer, the following condition is fulfilled:

$$\Delta \overline{F} = \Delta \overline{F}_m + \Delta \overline{F}_t = 0$$

where ΔF is the molar free energy of the monomers;

$\Delta \overline{F}_m$ is the osmotic component of the free energy of the monomer;

$\Delta \overline{F}_t$ is the component of the interphase free energy at the boundary between the polymer-monomer particle and the aqueous phase.

Using the well known formula of Flori and Hagbins [36], the molar free energy of a monomer can be determined as follows:

$$\Delta \overline{F}_m = RT \left[\ln (1 - V_p) + \left(1 - \frac{1}{\overline{n}} \right) V_p + \mu V_p^2 \right]$$

where V_p is the volumetric share of the polymer in the swollen particle;

$\overline{n}$ is the mean degree of polymerization;

μ is the polymer-monomer interaction parameter.

The value of $\Delta \overline{F}_t$ can be concluded from analysis of the increase in interphase surface as a function of particle size and interphase tension.

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$$\Delta \bar{F}_t = \frac{2V_m \sigma_{1-2}}{r}$$

where V_m is the volume of the monomer in the swollen particle, the share of the molar volume;

r is the radius of a polymer-monomer particle.

At equilibrium $\Delta F_m = -\Delta F_t$ and

$$\frac{2V_m \sigma_{1-2}}{RTr} = -\left[\ln(1-V_p) + \left(1-\frac{1}{n}\right)V_p + \mu V_p^2\right] \qquad (4)$$

As follows from equation (4), with a given particle radius and polymer content in the particle, a decrease in interphase tension helps to increase the volume of the monomer in the swollen particle, i. e., to increase the ratio of concentration of monomer to concentration of polymer [M]/[P]. This has been experimentally confirmed in [35-37], and also by the data presented in Table 1.1, in which it is shown that for more hydrophillic monomers, characterized by lower values of interphase tension, the ratio [M]/[P] in the polymer-monomer particles is significantly higher than for hydrophobic monomers.

Table 1.1. Influence of solubility of monomer in water on ratio of Concentration of monomer to polymer [31].

Monomer	Solubility of Monomers in Water at Various Temperatures			[M]/[P]	Biblio Ref
	T, °C	Wt.%	Molecules ·cm^{-3}		
Vinyl Toluene	45	$1,2 \cdot 10^{-2}$	$6,1 \cdot 10^{17}$	0,6—0,9	38
Styrene	45	$3,6 \cdot 10^{-3}$	$2,1 \cdot 10^{18}$	1,1—1,7	39
Chloroprene	25	$1,1 \cdot 10^{-1}$	$7,5 \cdot 10^{18}$	1,7	40
Bivinyl	25	$8,2 \cdot 10^{-2}$	$9,1 \cdot 10^{18}$	0,8	41
Methylmethacrylate	45	1,5	$9,0 \cdot 10^{19}$	2,5	31
Vinyl Acetate	28	2,5	$1,75 \cdot 10^{20}$	6,4	42
Methacrylate	45	5,6	$3,9 \cdot 10^{20}$	6,0—7,5	43

Depending on this, the rates of latex polymerization can be differentiated for polar and nonpolar monomers. Okamura and Motoyama [30] showed that the variation in the overall rate of polymerization of a monomer which is highly soluble in water -- vinyl acetate -- from the rate of polymerization described by equation (1) results only from its water solubility; if we equalize the solubility of styrene to the solubility of vinyl acetate by adding methanol to the aqueous phase, the rate of polymerization of styrene deviates from the rate described by equation (1) just as does the rate of vinyl acetate.

It follows from the above that the lower value of σ_{1-2} for more hydro-phillic (polar) monomers should in itself lead to a higher rate of latex polymerization (regardless of the reactivity of the monomer), but this factor decreases the adsorption of the emulsifier, i. e., the area of the polymer surface formed. Thus, competition arises between the rate of polymerization and adsorption of the emulsifier. The process of adsorption by the surface of the emulsifier particles, from the aqueous solution occurs at a high rate and is controlled by the rate of its diffusion to the surface. The growth of macromolecules in the polymerization reaction occurs practically instan-taneously and is also controlled by the diffusion of the monomer to the point of the reaction.

The formation of a stable colloidal dispersion of polymer occurs in the case of observation of proportionality between the rate of adsorption of the emulsifier, the surface of the polymer-monomer particles S and the rate of formation of this surface:

$$\frac{d\Gamma}{dt} = K \frac{dS}{dt}$$

where t is the duration of the process;

K is the proportionality factor.

With this concentration of polymer (or polymer-monomer particles), the value of surface formed is directly proportional to the number of particles formed N.

Therefore, formation of particles stabilized by the emulsifier requires that

$$\frac{d\Gamma}{dt} = K_1 \frac{dN}{dt} \tag{5}$$

where K_1 is the proportionality factor.

However, in actuality it may happen that

$$\frac{d\Gamma}{dt} < K \frac{dS}{dt}$$

and correspondingly

$$\frac{d\Gamma}{dt} < K_1 \frac{dN}{dt} \tag{6}$$

The mechanism of particle formation may differ depending on whether condition (5) is observed or not (Fig. 1.2). When this condition is observed (Fig. 1.2a), the polymer phase surface developed is stabilized by the adsorbed emulsifier and the particles formed may remain discrete with a significant consumption of emulsifier. If condition (5) is not observed, which may occur, for example, with low surface activity of the emulsifier on the polar surface of the polymer and high polymerization rate, particles appear with a surface

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not protected by the emulsifier. These particles, under conditions of high temperature and mixing, flocculate with each other rapidly, and complete adsorption of the emulsifier occurs on the latex particles formed (Fig. 1.2,b).
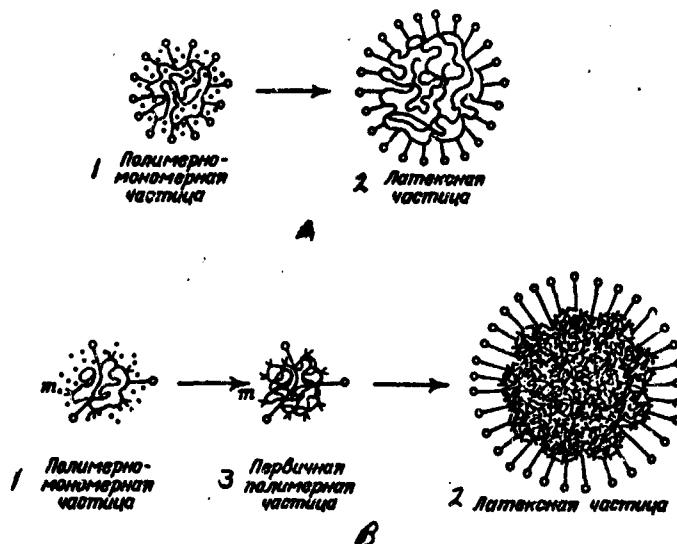
Fig. 1.2. Diagram of formation of latex particles during polymerization: a. nonpolymer monomers; b. polar monomers; 1. Polymer-monomer particles; 2. latex particle; 3. primary polymer particle.

Influence of Method of Performance of Polymerization on Polymerization Process

As was noted above, studies of the process of latex polymerization have been performed with the single-stage meth' of performance of the process, that is with simultaneous introduction of all reaction components to the reaction mixture. [1-19]. However, in certain cases it is expedient to produce latexes by continuous or semicontinuous methods. Recently, a number of works have appeared on the investigation of these methods of latex polymerization [26-28, 44-45].

It has been demonstrated that, by introducing the monomer to the reaction system simultaneously or gradually, the ratio of the rate of polymerization to the summary surface of latex particles v/S can be adjusted (Fig. 1.3). When the polymerization method is changed, the kinetics of formation of the latex systems, rate of polymerization mechanism of formation of particles and molecular weight of the polymer are changed. This has been established by comparative study of the polymerization of acrylic monomers (distinguished by their solubility in water) by three methods:

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1) single-stage polymerization, with simultaneous introduction of all reaction components at the beginning of the process;

2) semicontinuous polymerization, differing from the first method in that the monomer is dosed in gradually, as it is consumed;

3) Semicontinuous polymerization, differing from the first two methods in that both the monomer and emulsifier are added gradually in a predetermined ratio.


Duration of polymerization, min.
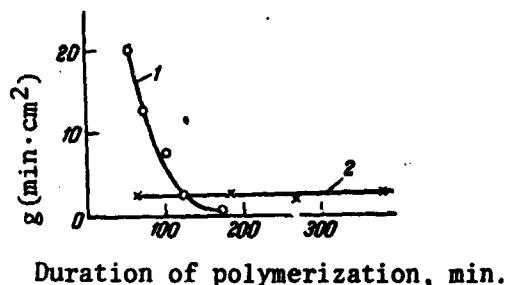
Fig. 1.3.   Change in v/S ratio during polymerization of acrylic monomers: 1. with simultaneous introduction of monomers;   2. with gradual introduction of monomer.

The initiator was introduced in all cases in three portions, as the process occurred. The recipe and temperature of polymerization were identical with all three methods.

The three methods produced three types of kinetic curves (Fig. 1.4). When the process was performed by the first method, the rate of polymerization was several times higher than for the other methods. This is obviously related to the higher concentration of monomer in the polymer-monomer particles. The process of polymerization by the second method occurs most evenly, and in practice it can be completely adjusted by changing the concentration of monomer in the system until the emulsion is formed. When the process is performed according to the third method, the rate of polymerization at the beginning of the process is lower than for the other methods, particularly for the more hydrophobic monomer -- butylmethacrylate, then it slightly exceeds the rate of polymerization corresponding to the second method, which probably results from accumulation of monomer in the system. This nature of increase in poly-merization rate in the initial stage for the third method can be explained by the insufficient concentration of emulsifier for micelle formation, which is apparently significant for polymerization of the hydrophobic monomer, since only in the case of colloidal solubility of the monomer in the micelles of emulsifier in the system are places formed where the concentration is high enough for the process to occur according to the mechanism of latex polymeri-zation.

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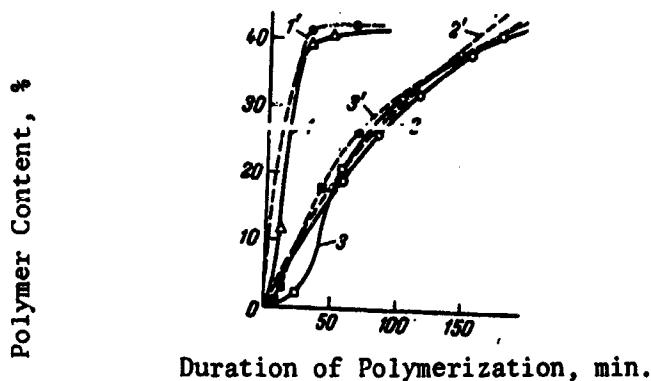
Fig. 1.4. Kinetics of Polymerization of Methylmethacrylate
with Butyl Acrylate (-----) and Butylmethacrylate (————)
Depending on the Method of Performance of the Process:
1, 1', Using first Method; 2, 2', Using Second Method;
3, 3', Using Third Method.
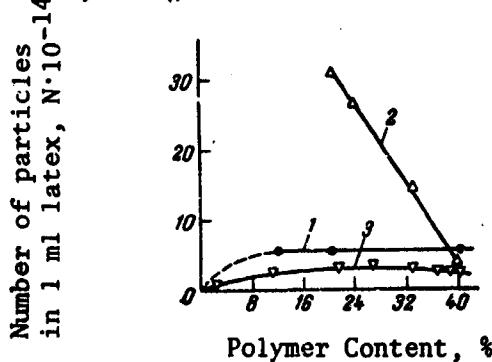
Fig. 1.5. Change in Number of Latex Particles During
Polymerization of Butylmethacrylate as a Function of
Polymerization Method: 1, First Method; 2, Second
Method; 3, Third Method.

In the process of polymerization using the first and third methods,
the number of particles does not change after a certain limit is reached
(Fig. 1.5), and, according to electron microscope studies, each particle
produced by the first method consists of an aggregate of primary particles.
This can be explained by the high rate of polymerization of the monomers
studied with the single-stage method under the conditions indicated in
table 1.2. Due to the high value of [M]/[P] in the particle, adsorption
of the emulsifier by the surface is preceeded by flocculation of the
particle, i. e., inequality (6) is correct. When polymerization is per-
formed using the second method, the number of particles formed at the
beginning of the process is many times greater than when the other methods
are formed, but it gradually decreases during the course of the process.
This is observed during polymerization of rather hydrophobic monomers and
in the case when the value of [M]/[P] during initial particle formation is
low, the process occurs rather slowly and the particles first formed ad-
sorb all the available emulsifier, i. e., condition (5) is observed. The

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particles of finished latex in this case are formed as a result of gradual flocculation of the primary particles formed at the beginning of the process, as can be seen from the electron photomicrographs shown on Fig. 1.6. This is apparently related to the fact that as the particle volume increases, the saturation of the surface with emulsifier decreases.
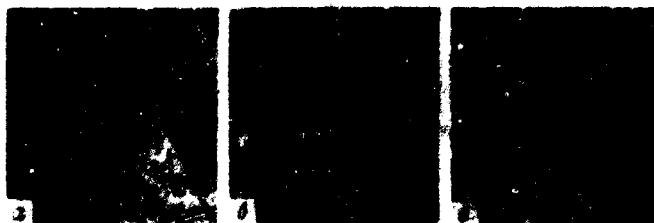
Fig. 1.6. Electron Microscope Photographs of Latex Particles Formed by Copolymerization of Methylmethacrylate with Butylmethacrylate (using second Method): a. Latex Concentration 8.3%; b. Latex Concentration 20.6%; c. Latex Concentration, 31.2%.

The total surface of polymer particles per unit volume S increases during the polymerization process of monomers little soluble in water according to the first method and remains constant with polymerization according to the second method (See table 1.2).

In the case of polymerization of monomers with significant solubility in water, the number of particles, even with gradual introduction of the monomers, remains constant; correspondingly, the total surface area of the particles increases during the process of polymerization. For these monomers, the rate of polymerization is so great that even with gradual introduction of monomer to the system, inequality (6) is fulfilled.

Decreasing the concentration of monomer in the reaction system, i. e., decreasing its content in the polymer-monomer particles, causes not only a decrease in the rate of polymerization (see Fig. 1.4), but also a decrease in the molecular weight (degree of polymerization) of the polymer, as follows from table 1.2.

The data of this table indicate that there is some real relationship between the degree of polymerization and the number of particles formed in the process of polymerization using the first two methods.

Thus, the graph of the dependence of the number of particles on degree of polymerization (n) of various polymers, constructed on the basis of the data of table 1.2 (Fig. 1.7) shows that with a latex concentration of 22-24%, corresponding to a conversion of 55-60%, this dependence is expressed by a curve described by the equation

$$N = \frac{K}{n^a}$$

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Since with this concentration of initiator, the degree of polymerization is proportional to the $\vdots$ lymerization rate, in the general case

$$N = \frac{K}{k_p^a [M]^a}$$

where k_p is the rate constant of the chain growth reaction.

For this monomer (when k_p=const)

$$N = \frac{K_1}{[M]^a}$$

Since at any given latex concentration the number of latex particles in one ml is inversely proportional to the volume of each polymer-monomer particle V, at the given emulsifier concentration in the system:
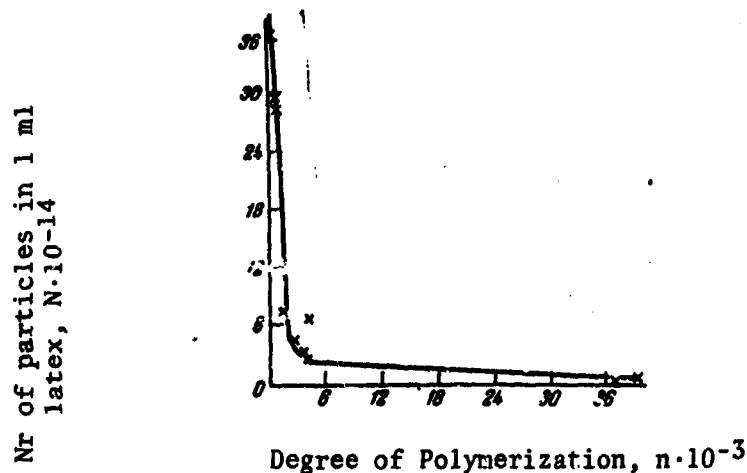
Fig. 1.7. Number of Latex Particles N as a Function of Degree of Polymerization n (According to Data of Table 2).

The empirical dependences presented allow us to draw some important practical conclusions: by changing the concentration of monomer in the particles by introducing monomer to the reaction mixture at various rates with a given emulsifier content, we can inf·uence the molecular weight of the polymer and the polymerization rate. Thus, a change in the rate of introduction of monomer to the reaction mixture as a function of its reactivity and solubility in water (determining the value of [M]) influences the colloidal properties of the latex and the molecular weight of the polymer formed.

When polymerization is performed by the third method, the process occurs with the same content of monomer in the system as by the second method, but the concentration of emulsifier is significantly less and is

Table 1.2. Kinetics of polymerization of various monomers at 72°C using first and second polymerization methods.

Monomers	Monomer Ratio, Wt. %	Polymerization Method	Latex Concentration, %	Monomer Content, % Beginning	Monomer Content, % At given latex concentration	Emulsifier Content (Sulfanol), %	Initiator Content (Potassium Persulfate, Mol)
Methacrylate Butylacylate, Methacrylic Acid	62:35:3	1	21,6 / 34,0	40 / 40	18,6 / 1,5		
			21,4 / 38,6	0 / 0	2,7 / 3,5	0,67	$\epsilon \cdot 10^{-4}$
		2					
Methylmethacrylate Butylacrylate	45:55	1	23,4 / 42,4	40 / 40	20,2 / 0,4		
			23,3 / 42,1	0 / 0	0,7 / 0,6		
		2					
Methylmethacrylate Butylacrylate Methacrylic Acid	42:55:3	1	23,4 / 39,6	40 / 40	19,2 / 0,1	1,33	$2 \cdot 10^{-8}$
			22,7 / 41,7	0 / 0	0,4 / 0,8		
		2					
Butylmethacrylate	100	1	21,2 / 41,0	40 / 40	19,5 / 0,9		
			24,3 / 42,5	0 / 0	0,4 / 0,8		
		2					

Table 1.2. Continued.

Degree of Polymerization $n \cdot 10^{-3}$	Polymer Particle Diameter, μ	Number of Particles in 1 ml Latex, $N \cdot 10^{-14}$	Total Surface of Polymer Phase in 1 ml latex, $S \cdot 10^{-3}$, cm^2	Monomers
36,8	0,19	0,5	64,8	Methacrylate
–	0,24	0,6	96,3	Butylacrylate,
3,1	0,12	2,4	109,4	Methacrylic
4,0	0,15	1,9	135,0	Acid
3,8	0,11	2,7	120,1	Methylmethacrylate
8,5	0,12	4,7	211,5	Butylacrylate
0,9	0,05	28,0	263,2	
1,8	0,10	8,0	248,0	
7,0	0,10	5,5	155,7	Methylmethacrylate
7,2	0,12	4,0	186,3	Butylacrylate,
0,8	0,05	28,8	256,0	Methacrylic Acid
1,5	0,10	5,4	191,0	
1,8	0,08	7,3	154,3	Butyimethacrylate
1,7	0,10	7,4	241,0	
0,3	0,05	36,6	202,0	
0,3	0,12	7,4	267,0	

equalized only at the end of the process. The number of particles formed does not change with polymerization by the first and third methods, in contrast to polymerization by the second method (see Fig. 1.4 and 1.5). From this we can conclude that the number of particles formed in the process of latex polymerization is determined by the relationship between the concentration of polymer and the concentration of emulsifier (or polar stabilizing groups in general) in the system.

The molecular weight of the polymer produced by the third method is somewhat greater than the molecular weight of the polymer produced by the second method (Fig. 1.8). One reason for this difference may be the increase in the time during which the reaction occurs at a high rate during polymerization by the third method.
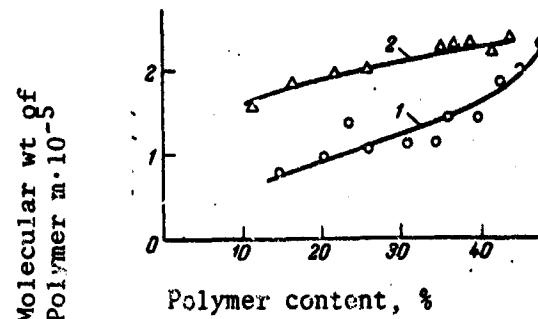
Fig. 1.8 Molecular Weight of Polymer as a Function of Content of Monomer with Various Methods of Performing the Process: 1. Second Method; 2. Third Method.

The data presented above can be practically utilized for mathematical modeling of continuous and semicontinuous methods of latex production. The composition of a universal mathematical model for all cases of latex polymerization is not possible, since these parameters may change significantly depending on the polarity of the monomer and the method of introduction of the reaction components to the reaction mixture. However, the use of mathematical methods and modern computer equipment to study the regularities of latex polymerization is of doubtless interest. The first attempts have been made on the basis of the regularities of polymerization in the simplest and best studies of polymerization systems, such as the model of the single-stage polymerization of the styrene monomer, which is little soluble in water, with an anionic emulsifier and water-soluble initiator [46], suggested by Harkins [4, 5] and mathematically studied by Smith and Ewart [12].

Polymerization Without Introduction of Emulsifiers

Latex polymerization in the presence of a specially introduced emulsifier produces a latex polymer contaminated with secondary material. The presence of the emulsifier also causes foaming of the paint and varnish materials and facilitates corrosion of metals. Therefore, there is interest in determining the possibility in principle of producing a colloidal stable latex without emulsifiers.

As was noted above, the stabilization of the polymer phase formed in the process of latex polymerization can be assured not only by its adsorption by the emulsifier, but also by the concentration of polar groups of macromolecules on the surface of the latex particles [47-49]. Latex can be produced without special emulsifiers if the concentration of polar groups on the surface of the particles is sufficiently high. The concentration of polar groups on the interphase boundary depends, on the one hand, on the value of the dipole moment or the degree of ionization, facilitating this concentration, and on the other hand, on the molecular weight of the polymer, which determines the degree of steric hindrance for movement of polar groups to the surface.

It is possible to produce concentrated stable, but rather low-molecular polymer dispersions by inhibited polymerization of a polar monomer-methacrylate-in aqueous phase without a special emulsifier [50]. This process forms particles of non-spherical shape measuring about 1,000 A in diameter, the stabilization of which is performed both by the polar groups of the macromolecular chains, and by the polar $-SO_4^-$ groups at the ends of the macromolecules included in them during initiation of polymerization by the persulfate. Latexes have also been produced without emulsifiers on the basis of another polar monomer -- vinyl acetate [51].

In practice, latexes without emulsifier are produced most expediently by copolymerization of ordinary hydrophobic monomers with monomers which are soluble in water due to the presence of ionizing groups. In this case, these groups have a sufficient stabilizing influence, and therefore the latexes can be formed not only by initiation with persulfate, but also when other initiators are used. Latexes without emulsifiers have been produced by copolymerization of lower alkyl acrylates with methacrylic acid [52] and with methylene methacrylamide [53, 54], and also by copolymerization of vinyl compounds with aminoalkyl methacrylate [55-58] and with sulfoethyl methacrylate [59]. It is characteristic that all of these water-soluble monomers in themselves have no significant surface activity; therefore, they should not be called copolymerizing emulsifiers, as some authors do. In the first stage of polymerization of such systems, beginning in aqueous solution due to the water solubility of the monomer and initiator, diphillic polymer radicals and polymers are formed, having high surface activity. The activation energy in this case is rather high, reaching a value characteristic for polymerization in solution [60]. Subsequently, the polymerization process is performed in the polymer-monomer particles, stabilized, on the one hand by the adsorption of surface-active polymer radicals and polymer homologues, and on the other hand by the polar groups of the polymer chains.

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For some latexes of low-molecular copolymers produced in this manner, it has been shown that the basic factor in stabilization is the dispillic nature of the macromolecules themselves, which have high surface activity, as a result of which they can be looked upon as a high-molecular analogue of ordinary surfactants [52]. Electrodialysis of these systems to the extent of complete removal of the low-molecular surfactant impurities (obviously formed in the initial stages of polymerization) does not change the colloidal stability and degree of dispersion of the latex. The colloidal stability of the latex is probably of primary significance in the case of latexes of higher molecular copolymers, for example the copolymer of butylmethacrylate with dimethyl methacrylate [57], [58].

Apparently, the possibility of "self-stabilization" of latex particles, the macromolecules of which contain polar groups, is beyond doubt. Actually, as was noted above, it has been demonstrated that even ordinary latexes, produced by initiation with persulfate in the presence of an emulsifier with complete removal of the emulsifier on ion exchange resins, remain colloidally stable.

Attempting to base himself on the position of the theory of Smith and Ewart, Van der Hoff [61], in studying persulfate-initiated poly-styrene with an emulsifier concentration below the critical concentration for micelle formation, assumed that the surface-active oligomers formed in the first stage of polymerization form complex micelles, in which the process of polymerization then continues according to ordinary mechanism suggested by these researchers.

However, it has been established that latexes produced without emulsifier are also formed in the case when the surface-active oligomers formed in the initial stages of polymerization are polyelectrolytes, i. e., non-micelle-forming surfactants.

In studies [58] of copolymerization of butyl methacrylate (BMA) with the acetic acid salt of dimythl aminoethyl methacrylate (DMAEMA) at pH 5.3 - 5.5, it was established that the surface tension at the water-air boundary σ_{2-3} drops sharply at the beginning of the polymerization process to 28.2 dyn/cm, then increases, reaching 63 dyn/cm in the finished latex (Fig. 1.9). It follows from this that copolymers are formed in the initial stage of the process, characterized by high surface activity, the content of which in the aqueous phase decreases as the process continues. Due to the ionization of hydrophillic (stabilizing) groups of these copolymers and the electrostatic repulsion which develops between them, we must assume that the copolymers formed act as non-micelle-forming surfactants.

The number of particles (curve 2) increases throughout the entire process of non-emulsifier polymerization, although much more sharply during the initial stages than during later stages, when the increase is very slight. The change in the composition of the copolymer during polymerization, enriched in the first stages by the water-soluble component, indicates the preferential

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occurrence of the process in these stages in the aqueous phase. In connection
with what we have said the initial mechanism of particle formation can be
looked upon as follows: When a given degree of polymerization is reached,
the polymer radicals formed in the aqueous phase precipitate and aggregate into
particles, in which polymerization occurs due to the monomer dissoved in them.
This mechanism is illustrated schematically on Fig. 1.10.
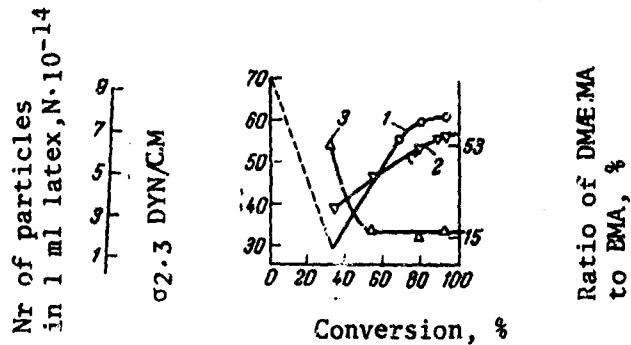
Fig. 1.9. Kinetics of Non-emulsifier Copolymerization
of Butylmethacrylate (BMA) with the Acetate of Dimethyl
Amino Ethylmethacrylate (DMAEMA): 1. Surface Tension
2. Number of Particles in 1 ml Latex; 3. Polymer
Composition.

In spite of the performance of the polymerization process without a
special emulsifier, all prepared "non-emulsifier" latexes contain a water-
soluble fraction, consisting of the same components as in the basic polymer.
This results from the fact that the initial polymerization process occurs
in the aqueous phase under the influence of the water-soluble initiator and
primarily involving the water-soluble monomer. Due to this, and also due to
the fact that the macromolecules of these latexes contain hydrophillic groups,
the coatings produced from them are unstable in water. However, if the
hydrophillic groups of the polymer are sufficiently reactive, such as
carboxyl or methyl groups, cross-linking of the polymer through these groups
can be used to achieve high water resistance. The problem of the practical
value of latexes produced without a special emulsifier must be solved in
the future.
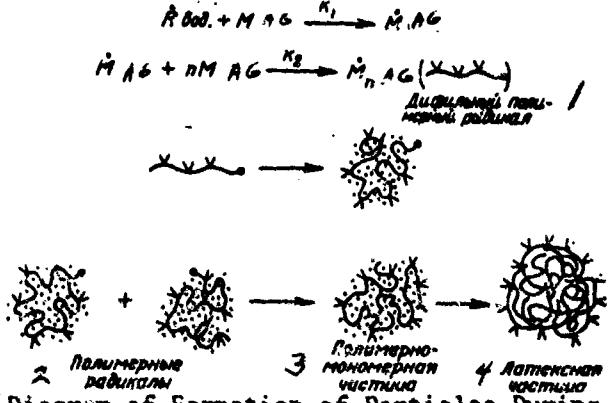
Fig. 1.10. Diagram of Formation of Particles During Emulsion Polymerization
Without Emulsifier. 1. Diphillic Polymer Radical, 2. Polymer Radical, 3.
Polymer-Monomer Particle, 4. Latex Particle, Bod=aq.

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Influence of Aqueous Phase on Structure of Latex Polymer

The process of formation of macromolecules in latex systems occurs in
the polymer-monomer phase with a very highly developed surface in contact
with the aqueous phase. The mean thickness of the layer in which the process
occurs is measured in hundreds of A, while the length of the developed macro-
molecules may reach some tens or hundreds of thousands of A. As the process
occurs in particles with a surface not saturated with adsorption layers of
emulsifiers, and also during synthesis of polymers containing polar groups,
there are sectors on the surfaces of the particles in direct contact with
the aqueous phase. In this case, the aqueous phase can have a direct influ-
ence on the structure, as well as the conformation and packing of the
macromolecules formed. Electron microscope photographs of latex particles
(Fig. 1.11) show that polymers with various functional groups, as well as
polymers produced with and without emulsifier, differ in their internal
structure and shape
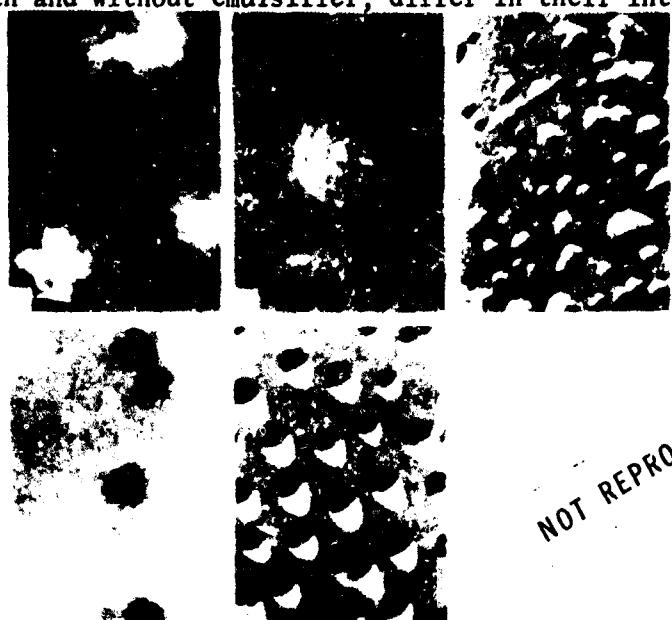
Fig. 1.11. Electron Microscope Photographs of Latex Particles: a, Alkyl-
acrylate Copolymers with Methacrylic acid Amide (1% emulsifier), 70,000 ×;
b, Copolymer of Alkylacrylate with Methacrylic Acid (1% emulsifier), 70,000 ×;
c, Polymer of Butylmethacrylate (5% Emulsifier), 40,000 ×; d, Polymer of
Methacrylate (Without Emulsifier), 40,000 ×; e, Copolymer of Butylmethacrylate
with Dimethyl Aminoethyl Methacrylate (without Emulsifier), 40,000 ×.

The influence of the aqueous phase is increased during copolymerization
of monomers with small quantities of monomers, significantly soluble in water
and containing hydrophillic functional groups (-COOH, $-CONH_2OH$, -OH, $-NR_2$
etc.).   This type of copolymerization modifies the latex polymers; they
are given better film-forming properties, high adhesion, a capability for
cross linking and corrosion resistance. The significant solubility of the co-
monomer in water gives it the ability to polymerize in the aqueous phase to an

extent. The extent to which the ability of the water-soluble monomer to polymerize in the aqueous phase in the presence of a water-soluble initiato. is realized depends on the coefficient of distribution between the hydrophobic monomer and the water. It has been demonstrated [62], that depending on the degree of dissociation, methacrylic and acrylic acid can be present at the monomer-water boundary primarily in two phases. The coefficient of their distribution between the two phases depends on the hydrophobicity of the monomer. In connection with this, copolymerization will form a copolymer with alternating links of both monomers or a block polymer of the acid and the basic monomer. Thus, the presence of the aqueous phase can determine the structure of the polymer macrochains formed.

As the emulsifier is introduced, the distribution of the water-soluble monomer between phases and the composition of the copolymer change in comparison to copolymerization without an emulsifier. This has been shown by studies of aqueous-phase copolymerization of ethylacrylate with methylene acrylamide [63]. During copolymerization under strictly identical conditions of alkyl acrylates with small quantities (5 wt.%) of water-soluble monomers, strongly differing in their distribution factor between the hydrophobic monomer and aqueous phases, latex particles are formed which differ clearly in their supermolecular structure (see Fig. 1.11a, b), which has a strong influence on the properties of the coatings produced from them. The presence of fibrilar orientation in the case of copolymers with methacrylate (see Fig. 1.11, a) leads to a sharp increase in the mechanical strength and water resistance of coatings in comparison with coatings based on copolymers with methacryllic acid.

Studies of the structure of films produced from latexes and solutions of the same polymers by the method of IR spectroscopy have shown that the degree of ordering differs, and have indicated that in the case of latex films, the interaction between the polar groups ($-COCH$, $-CONH_2$) due to formation of intermolecular hydrogen bonds, is realized to a greater extent (Fig. 1.12).

Thus, in the case of the carboxyl-containing copolymer, a greater intensity was noted of the absorption bands corresponding to the valence oscillations of the -OH group, bound by the intermolecular hydrogen bond, than for films produced from solutions (Fig. 1.12a). For the copolymer with methacrylic acid amide, the latex film shows fewer $-NH_2$ groups not bound with the hydrogen bond than in the film produced from the solution, which indicates the greater orientation of the macromolecules in the latex film (Fig. 1.12b).

Relating the results produced to the topochemistry of latex polymerization, we can assume that the conformation of the macromolecules formed on the boundary with the aqueous phase will differ, depending on the degree of polymerization of the groups contained in the macromolecules and the relationships between the intermolecular interaction and the hydration energy of the polar segments.

Electron microscope studies of latex particles and films indicate that the process of polymerization in ordinary adsorption unsaturated latexes is

-22-
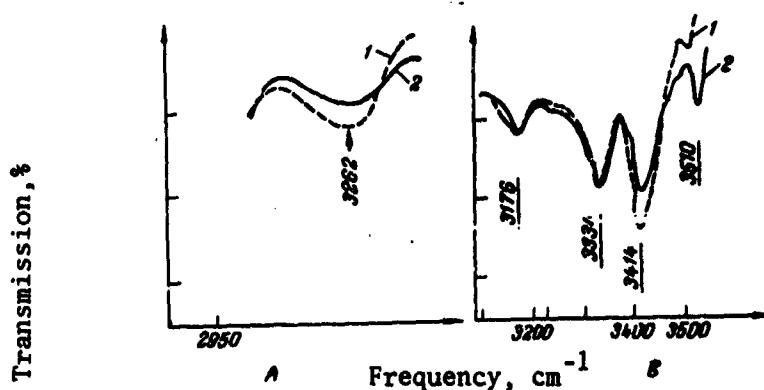
Fig. 1.12. IR spectra of Acrylate Copolymer Films: a. With 5% Methacrylic acid; b. With 5% Methacrylic Acid Amide; 1, from Latex, 2, From Polymer Solution.

performed not in the discrete latex particles, as is assumed in [1-5], [12-14], but rather in the smaller, primary particles, capable of being temporarily stabilized at the boundary with the aqueous phase, but flocculating in latex gobules as the process continues. This assumption is based on the complex structure of the globules observed under the electron microscope (see Fig. 1.6, c), particularly clearly seen after acid etching of specimens [63-69]. The structural element of the film is a globule of much smaller size than the latex particle. In the case of polymers which are in the state of viscous flow during the process of polymerization, the flocculation process of primary particles may be accompanied by a process of coalescence, in which case the primary particles will not be detected in the latex globule; the possibility of coalescence of particles increases with increasing [M]/[P] ratio in the particle, regulated by the method of polymerization. The primary particles are most clearly seen in the latex globule with the semicontinuous method of production of latex, with gradual introduction of monomers to the reaction mixture, when flocculation not of polymer-monomer, but rather of polymer ("dry") particles is observed.

Fig. 1.13. Electron Microscope Photographs of Latex Films Following Oxygen Etching (See Table 3): a. Copolymer of Methylacrylate with Butylacrylate; b. Copolymer of Methylacrylate with Butylacrylate and with 3% Methacrylic Acid; c. Copolymer of Methylacrylate with Butylacrylate and with 5% Methylacrylic Acid.

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It was established in this case that with identical consumption of emulsifier and identical latex particle size, the primary globules differ in size depending on the nature and content of polar groups in the polymer. Thus, in the case of latexes of polyacrylates and copolymers of the same acrylates with methacrylic acid, as the content of methacrylic acid in the copolymer decreases, the dimensions of the primary globules and the number of macromolecules which they contain decrease, as can be seen from table 1.3 and Fig. 1.13.

As the polarity of the polymer decreases and the consumption of emulsifier increases, the size of the latex particles decreases and, under certain conditions, may approximate the size of the primary globules. This is achieved, for example, in the case of butylmethacrylate latex (see table 1.3). In this case, no primary globules can be detected in the latex particles.

Thus, the various mechanisms of formation of latex particles depending on polarity of monomers and quantity of emulsifier used, schematically illustrated on Fig. 1.2, are confirmed by a study of the particle structures. Considering the results produced, we can draw a few conclusions concerning the topochemistry of latex polymerization of monomers which are highly soluble in water.

In the case of a water-soluble initiator, the process begins in the aqueous phase. When a certain degree of polymerization is reached, the polymer radicals $M_nSO_4^-$, formed in the aqueous phase, precipitate from the aqueous solution, aggregate into primary particles, are stabilized by the presence of polar groups ($-SO_4^-$, $-COOH$, $-COOCH_3$), and also adsorption by the emulsifier. The dimensions of the primary particles increase due to polymerization of the monomer which they absorb and their aggregation with other polymer radicals formed in the aqueous phase. Growth due to the latter of these factors obviously should lead to an increase in the number of macromolecules in a primary particle. However, the aggregation of primary particles with other polymer radicals should be progressively hindered with accumulation of dissociated groups, due to the increased surface charge density ($-COO^-$, $-SO_4^-$ groups) or hydrophillization of the surface (for example, $-COOCH_3$ groups in the case of polymethylacrylate); in connection with this, the number of macromolecules in the primary globule should gradually decrease. This has been experimentally confirmed by the results of experiments 1, 2, and 3, presented in table 1.3. The presence of unprotected sectors on the surface of the primary particles causes their flocculation with the formation of latex particles, stabilized by the polar groups and by adsorption layers of the emulsifier.

During polymerization of nonpolar, less active monomers, stabilization of the primary particles is achieved due to the emulsifier, more rapidly than by the polymer phase adsorbed on the nonpolar surface. Therefore, when saturation of the adsorption layer is achieved, further flocculation of particles does not occur (see experiment 4 in table 1.3).

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Table 1.3. Properties of latexes of Acrylic Polymers of various chemical composition.

Experiment No.	Latex Composition Monomers	Ratio of Monomers, wt. %	E-30 Emulsifier Content, %	Latex Particle Diameter, A	Primary Globule Diameter, A	Polymer Mol. wt., $M \cdot 10^{-5}$	Number of Macromolecules in Primary Globule
1	Methacrylate, butylacrylate	35.65	1	1130-2100	400	2.14	90-150
2	Methacrylate, butylacrylate, Mathacrylic Acid	32:65:3	1	1200-2200	250-300	2.03	25-40
3	Methacrylate, butylacrylate, methacrylic acid	30:65:5	1	1180-2000	150-200	2.27	5-11
4	Butylmetha-crylate	-	5	150-400	Not Detected	-	-

Notes: 1. Solubility of monomers in water at 20°C is: methylacrylate, 5.2%, butylacrylate 0.16%, butylmethacrylate 0.003%. 2. Ammonium persulfate used for initiation in all cases. 3. Primary globule diameter determined as distance between globule centers on electron photomicrographs of latex films. 4. Emulsifier -- sodium alkyl sulfonate.

The differences observed by many investigators in the dependence of polymerization rate on emulsifier concentration for monomers having different water solubility [22-24] can be explained by the factors described above. If stabilization of the primary polymer-monomer particles occurs in the case of significant water solubility primarily due to polar polymer groups according to the mechanism described above, the significance of the emulsifier in the polymerization process must decrease in comparison to monomers which are little soluble in water, which actually occurs.

CHARACTERISTICS OF LATEXES AS COLLOIDAL SYSTEMS

Latexes are lyophobic colloidal systems with disperse polymer phase particle dimensions of 0.01-0.2µ. Thus, the polymer in latex has a highly developed surface: for a latex with a particle diameter of 0.02µ, the specific polymer surface is 300,000 m^2/kg. This surface borders the aqueous phase through the adsorption layer of the emulsifier and directly [70]. It is assumed that the particles of latexes are generally spherical. However, in some cases they may have an ellipsoidal shape [71] or may be irregular in shape [50].
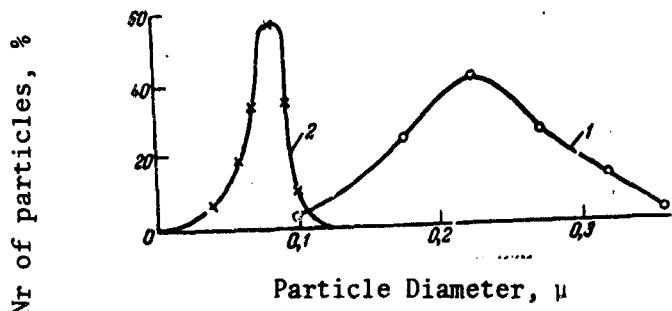
Fig. 1.14. Distribution of Particles by Size for Synthetic Film-forming latexes: 1. Copolymer of Methylmethacrylate with Butyl-methacrylate and 3% Acrylic Acid. 2. Copolymer of Chloroprene with Methylmethacrylate.

Most synthetic latexes are more highly dispersed and homogeneous in particle diameter than natural latex (the sap of the Brazilian rubber tree) the particle diameter of which fluctuates from 0.05 to 2µ. Figure 1.14 shows distribution of particles by diameter for certain synthetic film-forming latexes [72, 73]. The particle diameter with a given latex concentration influences its viscosity, as we can see from the data presented below [74]:

Mean diameter of latex particle, μ	0.096	0.171	0.325
Latex viscosity (60% concentration), cps	8,000	1,800	250
Latex concentration (viscosity 1,000 cps), %	55	59	63

The particles of latex are in a state of continuous Brownian motion. If we imagine that this motion is stopped at any moment and the particles of radius r are fixed in a nonmoving position, the statistical mean distance between them 1 would be [75]:

$$ l = \left[\left(\frac{710}{W} \right)^{1/3} - 2 \right] r $$

where W is the volumetric concentration of the latex, %;
r is the radius of the particles.

This formula can be used to calculate that with a latex concentration of 89 vol. %, the distance between particles becomes equal to 0, i. e., they come in contact. Most polymer dispersions coagulate at lower concentrations. Thus, for domestic acrylate and certain other latexes used in the leather industry [76], the critical concentration (wt. %) varies between 58 and 82 as we can see from the following data:

Acrylic emulsion
    A(STU 12-10-342--65)   82.0
    No 1 (STU 12-10-342--65)   63.5
    MBM-3 (TU 12-10-328--64)   73.0
Latex type DMMA-65-1 (STU 11-924--64)   69.0
Dispersion MKh-30 (MRTU 6-04-133--63)   58.0

In contrast to the stable, spontaneously formed lyophillic colloidal systems, latexes are thermodynamically unstable. All spontaneous processes in such systems are 1-directional and cause a reduction in the interphase boundary surface, i. e., a decrease in the degree of dispersion due to flocculation of particles or in the final analysis, coagulation, i. e., separation of the system into two volumetric phases with minimal division boundary surface. Thus, coagulation must be looked upon as a manifestation of aggregate instability of a thermodynamically non-equilibrium microheterogeneous disperse system. This indicates that the degree of aggregate stability is one of the most important characteristics of latexes.

Surfactants used for stabilization of latexes.

As was noted above, the stabilization of latexes is achieved by formation of protective adsorption layers of surfactants on the surface of the polymer particles, as a result of which the interphase surface tension is decreased.

Surfactants have a diphillic nature, i. e. they contain both a hydro-phobic and a hydrophillic group in their composition.

The hydrophillic group is usually either a group whicn disssociates in aqueous solution into ions (ionogenic emulsifiers) or a polygycol chain (nonionogenic emulsifiers). The hydrophobic portion of the surfactant molecule is a nonpolar alkyl chain with 9 to 18 carbon atoms, sometimes in-cluding an aryl radical.

Ionogenic surfactants can be divided into three main groups: anion-active (anionic), cation-active (cationic) and amphoteric. Typical repre-sentatives of anionic surfactants, most broadly used in the production of latexes, are fatty acid soaps and the sulfo-acids -- oleates, stearates, laurates, succinates, sulfonates, sulfonols and other compounds.

One characteristic feature of most soaps is their capability, even at low concentrations (10^{-3}-10^{-4} mol/l) of forming aggregates (micelles), con-sisting of associations of 50-100 molecules. Micellar solutions of soap are capable of increasing the solubility of hydrocarbons (solubilization) in water. Certain works on emulsion polymerization give this property of soaps great significance [2, 4, 5, 77-79].

Examples of cation-active surfactants include the salts of fatty amines or quarternary amonium salts, for example: cetyl trimethyl ammonium bromide $[(CH_3)_3-N-C_{18}H_{37}]+Br^-$, trimethyl carboxymethyl acetyl ammonium chloride $[(CH_3)_3-N-CH_2-COOC_{18}H_{37}]^+Cl^-$ and lauryl pyradine chloride [⬡ N-$C_{12}H_{25}]^+Cl^-$.

Amphoteric surfactants contain both basic and acid groups. Examples of such compounds include the fatty series derivatives containing basic and acid groups, for example, cetyl aminoacetic acid $C_{16}H_{33}-NH--CH_2COOH$ and alkyl aminosulfoacids $R-NH-C_2H_4-SO_3H$.

One important characteristic of surfactants is the relationship of the degree of manifestiation of hydrophillic and hydrophobic properties, called the hydrophillic-hydrophobic balance. This balance determines the type of emulsion formed.

There are several approaches to estimation of the hydrophillic-hydro-phobic balance [80-83]. The most reliable metnod is the experimental method, consisting in comparing the emulsifing capability of the emulsifier being studied with the emulsifing capability of a standard emulsifier having a known hydrophillic-hydrophobic balance; the more greatly the relationship of effectiveness of hydrophillic and hydrophobic groups in the molecule is shifted toward hydrophobicity, the higher the value of the hydrophillic-hydrophobic balance.

Nonionogenic [83-87] surfactants, in contrast to soap, are not capable of dissociating into ions in aqueous solutions. In most cases, these are organic compounds with a long hydrocarbon chain, hydrophillization of which

i. e., the property of being able to dissolve in water, is achieved by introduction to the molecule of a sufficient quantity of oxyethylene ester groups. The advantage of using this type of compound is the possibility of broadly varying their surface properties by adjusting the hydrophillic-hydrophobic balance [29, 80-87]. This is achieved by introduction to the molecule of oxyethylene segments of various links, and also by changing the molecular weight of the hydrophobic portion.

One example of nonionogenic surface active agents consists of the oxyethylated fatty series derivatives, as well as the alkylphenol derivatives, such as polyoxyethylated oleic acid $C_{17}H_{33}COO(C_2H_4O)_nH$, polyoxyethylated stearic acid amide $C_{17}H_{35}CONH(C_2H_4O)_nH$, polyoxyethylated alkyl phenol

C_9H_{19} $-\langle\bigcirc\rangle-$ $\vdash$ $-(C_2H_4O)_nH$,

as well as polyoxyethylene propylene glycol

$$OH(C_2H_4O)_l - (C_3H_6O)_m - (C_2H_4O)_nH.$$

One special category consists of the nonionogenic surfactants modified with polar groups.

Thus, sulfonated oxyethylated alkyl phenol with 8-12 carbon atoms or sulfonated oxyethylated fatty acids with 12-18 carbon atoms in the alkyl group are widely used as washing agents.[87]. The use of sulfonated oxy-propylated and oxybutylated fatty acids is promising [88-92]. Among the substances increasing the stability of dispersed systems, we must also note water-soluble high-molecular compounds such as polyvinylic acid, polyacrylic acid, a number of protein substances, as well as the solid surfactants. Mi-celles in the ordinary sense of this word do not exist in solutions of high polymers and polyvinylic alcohol [93], but each polymer molecule can be looked upon as the equivalent of a micelle and is the locus of polymerization as it occurs in the emulsion. The molecules of such substances as polyvinyl alcohol, in the aqueous phase, envelope the particles of the disperse phase in a thin surface film, which prevents joining of the dispersed phase parti-cles as they contact each other due to Brownian motion [94]. The effect of solids in the form of highly dispersed powders is also based on their con-centration on the surface of the dispersed phase due to selective wetting and the creation on the particles of the dispersed phase of a unique "shield-ing" envelope, preventing breakdown of the system.

Latex Stabilization Mechanism

In the overwhelming majority of cases, stabilization of dispersed phase particles is achieved by an interphase protective emulsifier layer. However, the structure and properties which the stabilizing interphase layer should have in order to protect latex particles from coalescing are still debatable. Various factors are noted to explain the stabilizing effects of adsorption layers [95-98].

According to one point of view, the aggregate stability of latexes is determined by the electric charge formed on the surface of globules by the ionogenic emulsifier, and the properties of the dual electric ion layer. The stability of lyophobic colloidal systems has been interpreted in a number of

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recent text books and monographs on the basis of the concept of the dual electric layer [99-101]. The proponents of the electric theory (Voyutskiy, Fervey, Overback, Kreut, etc.) base their arguments on the fact that colloidal particles, in particular globules of latex, are charged in relationship to the surrounding medium as a result of dissociation of the ionogenic emulsifier which they adsorb.

The presence of a charge (ζ-potential) on latex globules causes repulsion of like-charged particles, which are in continuous thermal motion, and is also the reason for the mobility of latex particles in an electric field and the high sensitivity to electrolytes.

Detailed studies have shown that a change in the ζ-potential of latex particles can result from the influence of electrolytes, the degree of dilution of the latex, the value of pH and dialysis; decreasing the ζ-potential causes a decrease in the aggregative stability of the system [95-106]. When the ζ-potential of the particles is near 0, latexes are aggregative stable.

The production of stable latexes in the presence of nonionogenic emulsifiers [105], having low ζ-potential [106-107], can be related from the standpoint of the electric theory of stability only to the presence of ionic impurities introduced to the latex as it is produced [108]. However, a number of experimental data have failed to confirm this concept. For example, Munro and Sexsmith [109] found that the stability of polyvinyl acetate latex, protected with mixed cation-active and non-ionogenic emulsifiers, does not always correspond to the change in its electrokinetic mobility, characterizing the value of the ζ-potential.

Roe and Brass [110] studied the dependence between the quantity of soap (potassium palmite) adsorbed by polystyrene latex and its mechanical stability measured by the time necessary for total flocculation of a latex specimen with strong agitation. The authors produced no direct dependence between stability of the latex to mechanical action and electrophoretic mobility of its particles. As the quantity of soap increased, the stability of the system increased sharply with unchanged electrophoretic mobility.

A more general explanation of the principles of lyophobic colloidal systems was developed in the works of Deryagin. This point of view was based on the conception of the presence of polymolecular layers of a medium, solvating the adsorption layer of the colloidal phase [111].

In studying the properties of thin layers of fluid, Deryagin, et al., [111-130] detected separating pressure in the interlayers of medium between two solids [111-130]. As the particles interacting with the dispersion medium approach each other, thinning of the layer of the medium occurs without a change in free energy only up to a certain point after which forces of repulsion which Deryagin called the layer separation pressure begin to act.

With a postive value of this separation pressure, a layer of the medium can only spontaneously grow thicker, i. e., it has thermodynamic stability and is a stabilizing factor. When there is no interaction between the molecules of the surface and the molecules of the medium, the separation pressure is practically equal to 0.

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The stabilization of dispersed phase particles, according to Deryagin, is achieved by lyophillization of their surfaces by creation of adsorption layers of oriented molecules of the surfactants or adsorption of ions from solution and creation of a dual electrical layer on the phase division boundary surface. In both cases, solvate layers of significant thickness arise around the particles of the dispersed phase, balancing the external forces attempting to bring the particles together with their separation pressure.

The theory of stability of lyophobic colloidal systems developed by Deryagin has been confirmed in a number of works by Soviet and foreign authors, dedicated to the study of synthetic latexes. It has been demonstrated [106] that the stability of latexes produced using nonionogenic emulsifiers decreases with increasing temperature, when dehydration of the stabilizer molecules occurs.

This viscosimetric studies have established the fact of hydration of colloidal electrolytes such as sodium lauryl sulfate, dodecyl ammonium chloride [131] and other fatty acid salts [132]. The authors of [133-135] also consider the factor of hydrophillization of the surface of colloidal particles to be the determining factor in stabilization by soaps and particularly by nonionogenic emulsifiers. The authors of [136] come to the same conclusion in their study of the stability of lyophobic silver iodide salts to the action of electrolytes.

One point of view concerning the reasons for the stability of colloidal systems, including latexes, is based on the concept of the structural and mechanical properties of the adsorption emulsifier layer produced by Rebinder [137-143]. According to this concept, one important factor in the stabilization of all lyophobic colloidal systems is a structural-mechanical barrier, present if the protective adsorption-solvate envelope has structural viscosity many times greater than the viscosity of the medium at low velocity gradient.

The mechanical strength of the adsorption layers of emulsifier becomes particularly significant with increasing concentration of the dispersed phase, when the electrical charge of particles is an insufficient stabilization factor. It is quite necessary in these cases to use materials forming rather strong 3-dimensional structures (such as gels) in the volume of the dispersion medium or on the surface of the dispersed phase particles. Cases of this strong stabilization are quite varied and represent a continuous transition from the formation of structures only in the adsorption layers through structuring of the entire volume of the dispersion medium. The increase in structural viscosity which occurs in this case, which is particularly great under conditions of an intact structural network, prevents the particles from moving together. However, the increase in the structural and mechanical properties of the adsorption layers cannot always be experimentally determined due to the breakdown of the structure.

The conception of the structural and mechanical factor in stabilization of colloidal systems has been developed in a number of experimental works [144-151].

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In the opinion of Trapeznikov [150], the mechanical strength of inter-
phase films increases with increasing saturation of the adsorption layer.
However, with limiting saturation of adsorption layers, the molecules lose
their mobility, causing a decrease in the elasticity of the adsorption
layers and a loss of their ability to repair ruptures. In this case, 70-80%
saturation of the adsorption layers is optimal [150-152].

In recent works on the mechanism of stabilization of concentrated hydro-
carbon emulsions [153-155], the opinion has been stated that the stabilizing
factor is the film of microemulsion, of identical composition with the macro-
emulsion. The microemulsion is formed on the division surface as a result
of quasispontaneous distribution of the emulsifier between the two phases.
The apparent lack of correspondence between the aggregative stability of
2-phase systems and the strength of the adsorption layers, which is sometimes
observed, can be eliminated if we consider the sharply hindered kinetics of
formation of surface stabilizing layers on the interphase division boundaries
during a change in structural and mechanical properties [154].

However, there are a number of works, the results of which do not agree
with the point of view of the predominant significance of the structural-
mechanical strength of the interphase layers. For example, in studying the
strength of the adsorption layer of a number of emulsifiers at the boundary
with air and with hydrocarbons, no parallelism was observed between the
mechanical properties of the interphase emulsifier layer and its stabilizing
ability [156].

A number of materials which are marvelous emulsifiers, for example,
sodium lauryl sulfate, do not form layers with high structural viscosity on
the hydrocarbon-water boundary surface [157]-[159], while various types of
saponin show a two-dimensional viscosity differing by millions of times with
identical foam life. Another indicator that the stability of emulsions and
latexes cannot be explained by the structural and mechanical properties of
the protective layers alone is the establishment by various investigators of
non-saturation [104, 160-165], gaseous nature [166-169] and low viscosity
[151] of adsorption layers of stabilizer.

Among the works dedicated to the stability of synthetic latexes, we can
note the studies of Neyman, et. al., [169-173]. In these studies, the
stability of dilute latexes is characterized by the kinetics of their coagu-
lation, evaluated by the nephelometric method according to change in turbidity
of a specimen, right up to full coagulation. The influence of electrolytes,
cation valence, dilution of latex and the degree of its adsorption saturation
on the kinetics of coagulation was studied. During the course of slow coagu-
lation under the influence of an electrolyte, the author noted two stages:
first of all, agglomeration of globules occurs, then this process is sharply
retarded, coagulation going over to a second, slower stage. The reason for
the retarding of initial agglomeration of globules during coagulation of
adsorption-unsaturated latexes is related by this author to the redistribution
of emulsifiers so that the initial contacts between globules lead to formation
of aggregates, the surfaces of which are covered by a saturated adsorption
layer of emulsifier. This completes the first stage of coagulation. The

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second stage occurs significantly more slowly than the first stage, a result of the necessity of overcoming the new potential barrier, resulting from the structure and properties of the surface-saturated adsorption-solvate film formed during the course of the first stage of coagulation. During coagulation of adsorption-saturated latexes, the second stage begins immediately. The study of the influence of polymer additives (for example, polyvinyl alcohol) [173] on the kinetics of latex coagulation has shown that this type of nonionogenic material is capable of increasing the stability of latex against the effects of electrolytes.

The authors assume that the aggregative stability of synthetic latexes, stabilized with ionogenic emulsifiers, is determined by the presence and joint action of two protective factors, with the electrostatic factor [171] predominating during the first stage, the structural-mechanical barrier of the adsorption layer predominating in the second stage. Apparently, this results from the fact that many latexes have good stability in the presence of a mixture of ionic and nomogenic emulsifiers [109, 174-177].

The concepts of two stages of coagulation are applicable also to hydrodispersions of titanium dioxide [174], indicating the generality of the mechanism of coagulation of colloidal systems regardless of the nature of their dispersed phase and stabilizer.

During the process of manufacture of paint and varnish materials, their storage and application, coagulation of latexes may occur under the influence of various factors:

1) Addition of polyvalent metal salts, acids, dispersions with oppositely charged particles, as well as water-soluble organic fluids such as acetone, alcohol, etc.;

2) Strong dilution of the latex;

3) Freezing;

4) Heating;

5) Evaporation of the water;

6) The action of an electric current;

7) High pressure or shear stresses;

8) Introduction of finely dispersed materials capable of changing the adsorption equilibrium in the system.

Systematic studies of the influence of various factors on the aggregative stability of latexes were performed by Lebedev, et. al., [132, 178-181]. The results of their studies have shown that no single factor can be responsible for the aggregative stability of latex to various types of actions, and that the coagulation mechanism under the influence of these factors is

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also different. For example, the change in the stability of latex upon introduction of electrolytes, upon freezing-thawing, under mechanical loads, upon introduction of mineral fillers, upon long storage, etc. differs in nature.

The mechanical stability of latexes increases sharply with increasing concentration of emulsifier in the protective layers [88-89], etc., and also with increasing length of the emulsifier chain (fatty acid soap) [179, 185], which speaks in favor of the structural-mechanical factor of latex stability to this type of factor.

Great significance is given to the electrostatic factor in the stability of latexes stabilized by ionic emulsifiers; this factor determines their insufficient stability to the effects of electrolytes. Latexes stabilized with nonionogenic emulsifiers, in which the main stability factor is the hydration of the adsorption layers of the emulsifier, have high stability against the effects of electrolytes.

The stability of latexes to the effects of mineral pigments, in contrast to their stability to mechanical actions, is related not only to the degree of saturation of the globule surfaces with emulsifier, but also to the ability of the pigment particles to be adsorbed by the emulsifier, since in this case desorption of the soap from the surface of the latex globules may occur.

Particularly rigid requirements must be placed on the adsorption protective layer of polymer globules during freezing and thawing of latexes. The authors believe that in this case the interphase layers of the emulsifier must be, on the one hand, as strongly hydrated as possible and, on the other hand, firmly bonded to the polymer. Therefore, one effective means for increasing the stability of latex to this sort of action is grafting of materials increasing the hydrophillic properties of the polymer molecule to the main polymer, in particular molecules of methacrylic acid [179].

In [90], the authors also state that the stability of latex can be increased by copolymerization with water-soluble monomers, such as acrylic and methacrylic acid, which become unique, built-in stabilizers.

The stability of latexes to heating and long-term storage, in the opinion of the authors of [179], is also determined by the degree of adhesion of the emulsifier with the polymer.

When latexes are stabilized, it is necessary to consider the properties of the polymer phase surface, determined by the nature of the monomer and the initiator used in production of the latex. However, this factor has not yet been given sufficient attention. The stability of latexes can be determined to a significant extent by the polar group of macromolecules located on the surface of the globules. These groups may be present in the macromolecules of the polymer as residues of the initiators [50] or may arise during oxidation.

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During polymerization of monomers containing polar groups, the macro-
molecules of the polymer are oriented so that the polar groups are located
primarily on the surfaces of the globules [64]. In these cases, the surface
of the polymer particles is characterized by a mosaic structure with alter-
nating polar and nonpolar sectors. The globules, without emulsifier, may
have the shape of spheres with extended polar outgrowths, formed in the
aqueous phase [50] (see Fig. 111d).

Since the adsorption of surfactants by the polymer surface occurs as
a result of concentration of surface energy on the interphase division
boundary, it should be expected that adsorption will be easier in the case
of a nonpolar polymer. Actually, stabilization of latexes produced on the
basis of monomers little soluble in water such as styrene, butadiene, iso-
prene, etc., is easier than in the case of monomers with good water solubi-
lity. Therefore, different emulsifiers are required for each type of monomer.
In most cases, latexes based on monomers which are highly soluble in water,
in particular polyvinyl acetate monomers, are produced using high-molecular
protective colloids as stabilizers, for example, polyvinyl alcohol, methyl
cellulose, hydroxyethyl cellulose, as well as high-molecular nonionogenic
surfactants [90, 92]. Mast, Fisher, et. al., in a series of works [186-188]
dedicated to the study of emulsion polymerization of acrylic esters, emphasize
particularly the specifics of stabilization of these latexes [85-86]. It
has been found that soaps are poor emulsifiers for these monomers: latexes
have low stability, low dry residue and a significant quantity of polymer
precipitates as a coagulum during the process of synthesis. The most effec-
tive emulsifiers were sulfonated products such as sulfonates and sulfonols
(particularly mixed alkyl-aryl sulfonates). Good results in the synthesis
of concentrated, stable latexes based on lower alkyl acrylates were produced
by using various combinations of sulfo-products with nonionogenic surfactants,
which do not produce positive results alone.

Quantity of emulsifier, % (of monomer).
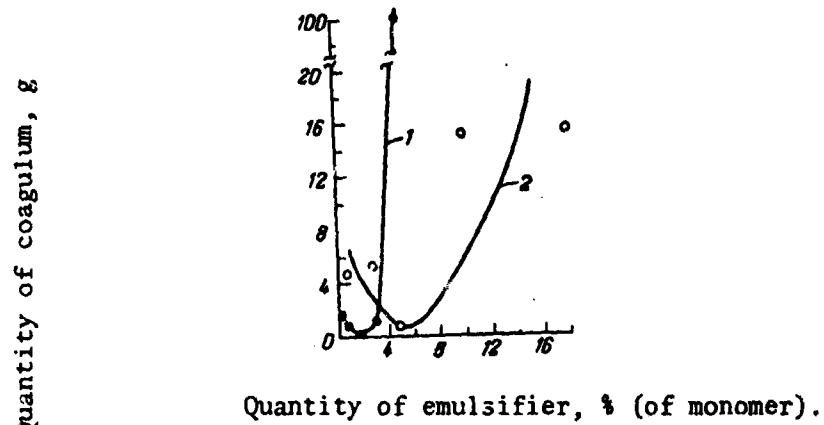
Fig. 1.15. Quantity of Coagulum as a Function of
Quantity of E-30 Emulsifier Introduced During Latex
Polymerization: 1. Methylacrylate; 2. Butylmethacrylate.

-35-
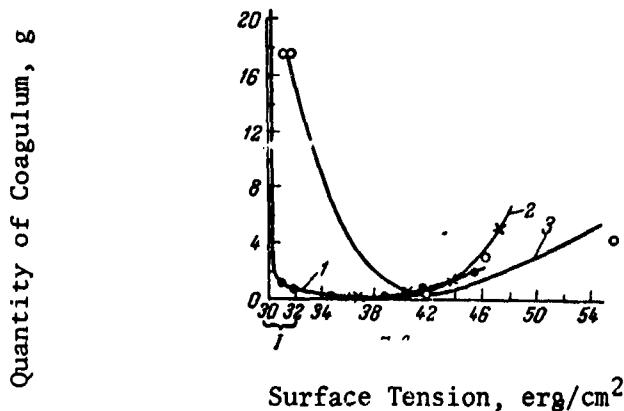
Fig. 1. 16. Quantity of Coagulum as a Function of Surface
Tension During Latex Polymerization: 1. Methylacrylate
with E-30 Emulsifier; 2. Methylacrylate with S-10 Emulsifier;
3. Butylmethacrylate with E-30 Emulsifier.

The regularities which occur during emulsion polymerization of a
monomer which is highly soluble in water such as methacrylate have also been
extensively studied. [33, 189].

A study of the polymerization of butylmethacrylate (little soluble in
water) and methylacrylate (significantly soluble in water) in the presence
of E-30 emulsifier and persulfate as an initiator showed (Fig. 1.15) that
in both cases there is an optimal quantity of emulsifier, above which coagu-
lation of the latex occurs [190]. In the case of the polymerization of
methylacrylate, it is 0.5-5%, while in the case of butylmethacrylate it
reaches 10-20%. Consequently, the presence of the optimal quantity of
emulsifier is a general regularity for the process of polymerization of
these two types of monomers, initiated by persulfuric acid. The lack of
data on the maximum concentration of emulsifier for the case of polymeriza-
tion of monomers little soluble in water can be explained by the fact that
this maximum lies in the area of very high concentrations, where the process
of emulsion polymerization is generally not performed.

A decrease in the stability of a latex occurs when the critical concen-
tration of micelle-forming emulsifier is reached in the aqueous phase of
the latex, i. e., when micelles of the surface-active agent are present in
the solution. The decrease in stability of the latex following attainment
of the critical concentration for micelle formation by the emulsifier can be
related to the formation of polymolecular adsorption layers on the surface
of the polymer particles, leading to aggregation of the particles [191-193].
The influence of the transition of the emulsifier solution from a true
solution to a colloidal solution on the stability of latexes is clearly
shown on Fig. 1.16; this figure shows the dependence of the quantity of
coagulum on surface tension at the polymer-water boundary, which changes
right up to the critical concentration of micelle formation.

Quantity of Emulsifier, %
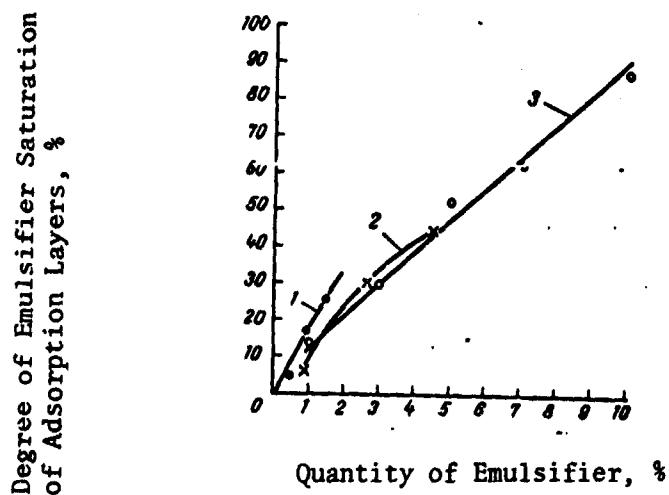
Fig. 1. 17. Degree of Saturation of Adsorption
Layers of Latex Particles as a Function of Quantity
of Emulsifier for Latexes Based on: 1. Methylacrylate
with E-30 Emulsifier; 2.Butylmethacrylate with E-30
Emulsifier; 3. Methylacrylate with S-10 Emulsifier.

The degree of saturation of adsorption layers of the latex particles
with emulsifier increases with increasing quantity of emulsifier both for
polymethylacrylate and for polybutylmethacrylate latexes, but for the latter,
the degree of saturation is significantly higher (Fig. 1.17). The degree
of saturation of polymethylacrylate does not exceed 27%, while polybutyl-
methacrylate latexes have a higher degree of dispersion.

We can conclude from the data presented that the use of anionogenic
emulsifiers for emulsion polymerization of monomers which are significantly
soluble in water does not provide for the production of stable latexes.

Quantity of Emulsifier, % (of monomer)
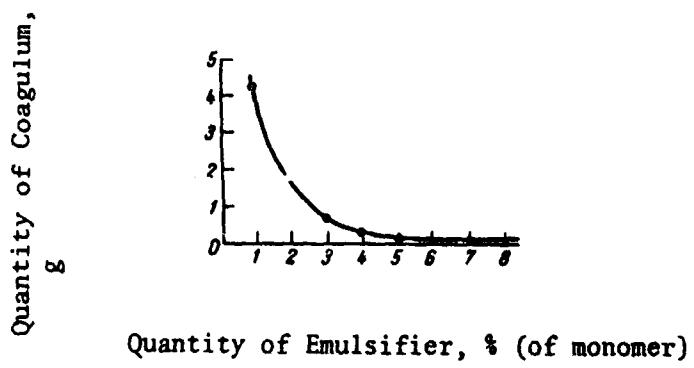
Fig. 1. 18. Quantity of Coagulum as a Function of
Quantity of S-10 Emulsifier During Latex Polymerization
of Methylacrylate.

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Bondy [92] believes that adsorption of highly charged molecules on the polymer-water boundary is always limited by forces of repulsion arising between the charged groups. Therefore, when anionogenic emulsifiers are used, a high degree of adsorption saturation is never achieved, in contrast to nonionogenic surfactants, which allow the production of adsorption-saturated latexes. When nonionogenic and anionogenic surfactants are used together, high stability of latexes is achieved, since the molecules of the nonionogenic surfactants can fill the intervals on the polymer surface not fully covered by the adsorbed anionogenic emulsifier.

The production of special emulsifiers combining the properties of anionogenic and nonionogenic emulsifiers is of great interest for the synthesis of colloidally stable latexes based on monomers with good water solubility. It is assumed that the adsorption of such an emulsifier on the polar polymer surface, due to the presence of nonpolar hydrophillic sectors in its molecule, will be more complete and will make possible the production of a sufficiently saturated protective emulsifier layer on the particle surface [91, 92].

For example, the ammonia-neutralized product of sulfonation of oxyethylated alkylphenol (S-10 emulsifier) supports the production of stable concentrations of latexes based on methylacrylate and other alkyl acrylates, as well as their copolymers with vinyl acetate. In the case of polymerization of methylacrylate, a significant increase in the concentration of this emulsifier does not cause coagulation of the latex, as can be seen from Fig. 1.18. Up to an emulsifier concentration of 7%, the stability of the latex increases, after which it remains constant [194]. The achievement of the critical concentration for micelle formation of this emulsifier in latexes does not reduce their stability, in contrast to E-30 emulsifier (see Fig 1.17, Curve 2). When the quantity of S-10 emulsifier in the system is increased, the saturation of the adsorption layers of latex particles increases (see Fig. 1.17, Curve 3). These data indicate that the adsorption of this emulsifier by the surface of the polymethylacrylate is facilitated. As the quantity of S-10 emulsifier is increased, the rate of polymerization of the methylacrylate is decreased (Fig. 1.19), this rate being significantly lower than in the case of the use of E-30 emulsifier.
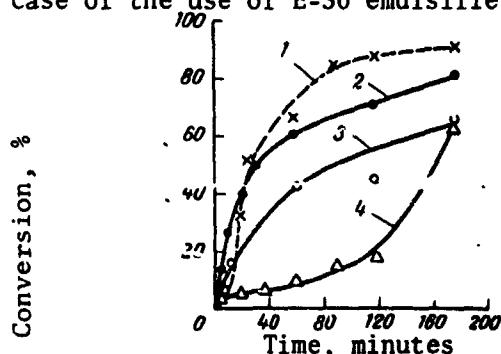
Fig. 1.19. Kinetics of Polymerization of Methylacrylate: 1. With 15% E-30 Emulsifier; 2. With 3% S-10 Emulsifier; 3. With 5% S-10 Emulsifier; 4. With 7% S-10 Emulsifier.

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We can assume that the relationship of rates of polymerization of the monomer and adsorption of the emulsifier by the polymer surface is an important factor in emulsion polymerization, determining the colloidal stability of the latex systems.

Mechanism of Formation of Latex Coatings

Although the drying of a polymer solution of any degree of hardness always forms a film, the production of a continuous latex film requires that certain conditions be observed. This results from the fact that the polymer in the latex is not distributed in the form of more or less associated molecules, but rather in the form of particles, sometimes containing tens of thousands of macromolecules. Combination of blocks into a continuous film involves surface phenomena at the division boundary between particles and water and is related to the mobility of the macromolecules which the particles contain. Therefore, the mechanism of film formation of latexes has been the subject of a number of special studies. Several assumptions have been stated in the published works concerning the sources of the energy which binds the latex particles into a continuous, single-phase film.
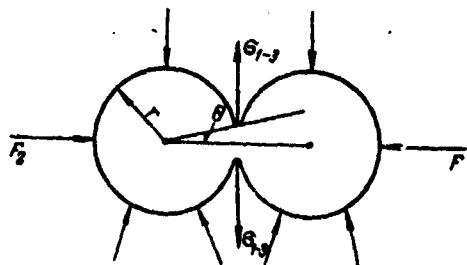
Fig. 1.20. Diagram of Interaction of Forces Facilitating Coalescence of Latex Particles.

Thus, in some studies [195-197], the surface tension at the polymer-air boundary, which tends to decrease the surface of the polymer phase, is taken as the motive force for film formation. It is assumed that following evaporation of water, the dry latex particles flow together under the influence of the force of surface tension, which depends on angle θ (Fig. 1.20), the value of which is determined from the equation of Frenkel' [198]:

$$\theta = \sqrt{\frac{3\sigma_{1-3} t}{2\pi\eta r}}$$

where σ_{1-3} is the surface tension at the polymer-air boundary;
  t is the particle contact time;
  η is the viscosity of the polymer;
  r is the radius of a polymer particle.

Van der Hoff and Bradford [199-200] came to the conclusion that the source of energy during coalescence of flocculated particles submerged in water is the surface tension at the polymer-water boundary; in this case, angle θ (see Fig. 1.20) cannot exceed 30°.

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Until recently, the most popular theory has been that of Brown [201], according to which the main motive force for the process of film formation consists of capillary forces arising as a result of the negative curvature of the water-air division boundary in the capillary system formed during the process of drying of a film. Brown believes that surface tension at the polymer-air boundary cannot be the motive force of the process, since the formation of a continuous film of latexes occurs in an aqueous medium and ends when the evaporation of water is completed. On the other hand, surface tension at the polymer-water boundary, fluctuating within limits of 0-10 dyn/cm, is quite low; therefore, it is a secondary factor in the process of film formation.

The capillary pressure F_1 can be determined from the formula

$$F_1 = \frac{2\sigma_{2-3}}{r_\kappa} \qquad (7)$$

where σ_{2-3} is the surface tension at the boundary between the aqueous phase and the air;

r_k is the radius of a capillary between latex particles.

Calculations have shown that $F_1 = \frac{12.93\sigma_{2-3}}{r}$.

Assuming that the layers of water between latex particles are cylindrical, (Fig. 1.21A), it is easy to find the radius of a capillary using the formula:

$$r_\kappa = \frac{r(1 - \cos 30°)}{\cos 30°}$$

where r is the radius of a latex particle.

According to Brown, the film formation process occurs when

$$F_1 + F_2 + F_3 + F_4 > F_5 + F_6$$

where F_1 is the force of capillary pressure;
F_2 is a force dependent on surface tension at the polymer-water boundary;
F_3 are the forces of intermolecular interaction;
F_4 is the force of gravity;
F_5 is the deformation resistance;
F_6 is the force of electrostatic repulsion.
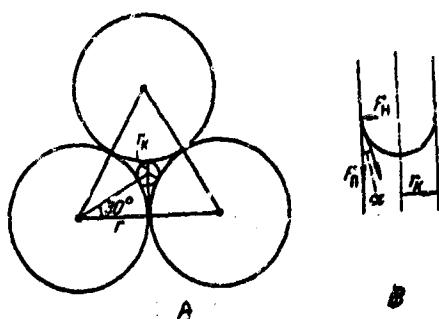
Fig. 1.21. Diagram of Development of Capillary Forces During Drying of Latex: a. Diagram of Development of Capillary Forces; b. Diagram of Resolution of Capillary Forces.

Brown gives decisive significance to capillary pressure F_1 and deformation resistance F_5.

We know that the deformation resistance of a thermoplastic polymer depends on temperature. Therefore, a number of works [202-204] use the concept of "minimum film formation temperature"(MFT), i. e., the temperature, above which the globules of a thermoplastic polymer can deform to form a continuous film. The MFT is an important characteristic of a film-forming latex. It is assumed that it corresponds to the temperature of transition of the polymer from the glassy state to a highly elastic state. As we know, increasing the plasticity of a rigid polymer to a certain degree by introducing a plasticizer or increasing the film-formation temperature helps to produce more homogeneous coatings.

Fitch [205], in studying Brown's theory, assumed that under ordinary conditions of film formation, surface tension at the water-air boundary is of primary importance; as the temperature increases and the water evaporates rapidly, probably, a primary role is played by surface tension at the polymer-water boundary, to which he also attaches great significance. Recent works have made significant modifications in the concepts of Brown. For example, it has been shown that the dimensions of particles, which should determine the value of capillary forces, have no influence on the film-formation process [48,55]. On the other hand, Sheetz [55], analyzing the concepts of Brown, concludes that water is fed to the surface not only through capillaries, but also through the latex particles themselves. this connection, he assumes a diffusion-osmotic mechanism of film formation. Sheetz bases himself on the assumption that for actual latexes the surface tension at the aqueous phase-air boundary is over 30 dyn/cm and that wetting angle α is greater than 0. Therefore, the force applied to the wall of a capillary can be resolved into 2 components, as is shown on Fig. 121b.

Force $F_n = 2\pi r_k \sigma_{2-3} \cos \alpha$, perpendicular to the surface and directed into the volume of the film, applies compressing pressure onto the particles, while force $F_H = 2\pi r_k \sigma_{2-3} \sin \alpha$ tends to cover the apertures of the capillaries and therefore to close the surface of the film with polymer.

-41-

With permissible values of σ_{2-3} $F_H > F_n$. Thus, under the influence of capillary forces in a moist latex film, compression and deformation of the particles within the volume of the film are accompanied by a decrease in porosity of the surface layer.

The polymer film formed on the surface of drying latex is permeable for water vapo., but not for liquid water; this produces the osmotic pressure, directed into the film and tending to compact its structure.

To prove the diffusion-osmotic mechanism of the process, the author compared film formation from a layer of latex covered directly with a thin-film of vapor-permeable polymer and by the same film, located at some distance from the latex layer; observations showed that in the first case, a transparent film was formed, in the second case -- a turbid and poorly coalesced film. Evaporation of moisture through the polymer particles is also confirmed by the fact [55] that the process of film formation from a hydrophillic polymer latex (methylmethacrylate and butylacrylate polymer) occurs at a higher rate than formation of a film from a hydrophobic polymer latex (butylacrylate and vinylidene chloride polymer).

A similar regularity was detected in another work in studying the kinetics of the film-formation process from polymers differing in their polarity [206], as well as copolymers of alkylacrylates containing various functional groups [207].

The possibility of evaporation of moisture through latex particles is apparently confirmed by the data of [208], showing greater mobility of the macromolecules in latex particles than in films; this may be related to the presence of water in the latex particles.

Sheetz calculated the work necessary to produce a unit volume of film from latex of known concentration, and compared it with the effectiveness of various energy sources necessary for film formation. Among these sources he includes the energy of evaporation of water and the polymer-aqueous phase surface energy. As a result, Sheetz concluded that only the energy of evaporation of water could be sufficient for this work. In this connection, he believes that the primary source of energy for film formation is the heat surrounding the medium, converted into useful work by evaporation of water through the latex particles; during the first half of the process, capillary forces and surface tension at the polymer-water boundary are also significant [199, 200, 209).

Of all existing concepts of the mechanism of film formation from latexes [210], we must give preference to the diffusion-osmotic mechanism of Sheetz.

As concerns film formation from filled latex systems, this problem has as yet been little studied. Data have been presented indicating that upon pigmentation of dispersions, the minimum film-forming temperature is increased by 5-12°C as a result of placement of the pigment between polymer particles and decreased capillary forces [205, 211, 212]. In order to decrease the influence of pigments, it is recommended that coalescing materials be introduced

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temporarily plasticizing the polymer and decreasing the minimum film-forming temperature. Some of these, such as cellosolvacetate, are quite effective even when added in quantities of 2-4% of the mass of the latex.

These concepts provide us with a general picture of film formation and qualitatively describe its possible mechanisms. However, these concepts greatly simplify the very complex physical and chemical process and do not indicate the relationship between the properties of latexes and latex films.

Apparently, there is reason to believe that the following factors should have decisive significance in the process of film formation from latexes and in determining the properties of the films formed, resulting to a significant extent from their structure: The physical state of the polymer, its chemical structure, the content of emulsifier and the fine structure of the latex particles.

Influence of Physical State of Polymer on Film-Formation Process

As follows from the conceptions of Brown and from the fact of existence of a minimum film-forming temperature, a continuous latex film is formed only at a certain minimum value of the modulus of elasticity (deformation resistance) of the polymer. It is considered that the formation of a latex film can occur at any temperature higher than the glass-transition point of the polymer. This is explained by the fact that in latex, due to the tremendous surface of the polymer, some of the macromolecular segments on the surface of the particles is not subjected to interaction between segments. When the latex particles contact each other, mutual penetration of the macromolecular segments located on their surface and having significant freedom of rotation may occur, as a result of which the process of film formation may be realized at temperatures below the glass-transition point determined for the polymer in a block. Therefore, it is assumed that the temperature at which the film-formation process occurs must be a function of the ratio of surface to volume of the polymer phase.

Investigation [165] of the film-formation process with acrylic polymer latexes of various hardnesses (synthesized under identical conditions), has shown that the formation of a continuous film occurs only up to a certain critical value of modulus of elasticity (about 30kg/cm^2). This can be clearly seen from Fig. 1.22, showing photographs of acrylic polymer films of various hardnesses. In the case of a rather soft copolymer, a homogeneous film is formed (see Fig. 1.22a); as hardness of the polymer increases, internal stresses develop in the film and cracks are formed (see Fig. 1.22b).

With further increases in hardness, coalescence of the particles into a continuous film does not occur (Fig. 1.22c).

The physical state of the polymer determines not only the possibility of film formation but also the kinetics of the film-formation process [213]. This is confirmed by the data of [206], presented on Fig. 1.23, on the kinetics of film formation from latexes based on copolymers in the highly elastic

-43-

state (copolymer of ethylacrylate with methylmethacrylate and methacrylic acid) and in the state of viscous flow (copolymer of ethylacrylate with methacrylic acid). The tangent of the angle of inclination tan β of each linear sector of the curve can be used to characterize the rate of occurrence of the film-formation process at this stage. During the process of film formation from a highly elastic copolymer, 2 clearly expressed breaks on the curve of water content in the latex are seen: at point a, the rate of film formation increases, while at point b it decreases. The similar curve for the viscous flowing copolymer has a single break: at point c, film formation is retarded. As has been established, the increase in the rate of film formation from highly elastic copolymers is observed with a latex concentration of 71-80% [206]. This concentration corresponds approximately to the critical concentration, at which the latex particles lose their mobility and the capillary structure is developed. The increase in rate of film formation, according to the conceptions of Brown, can be explained by the development of this structure; its walls, on the one hand, prevent passage of electrical current, while on the other hand, as they compress, they expel the water remaining in the capillaries to the surface of the system, facilitating an increase in the rate of evaporation.
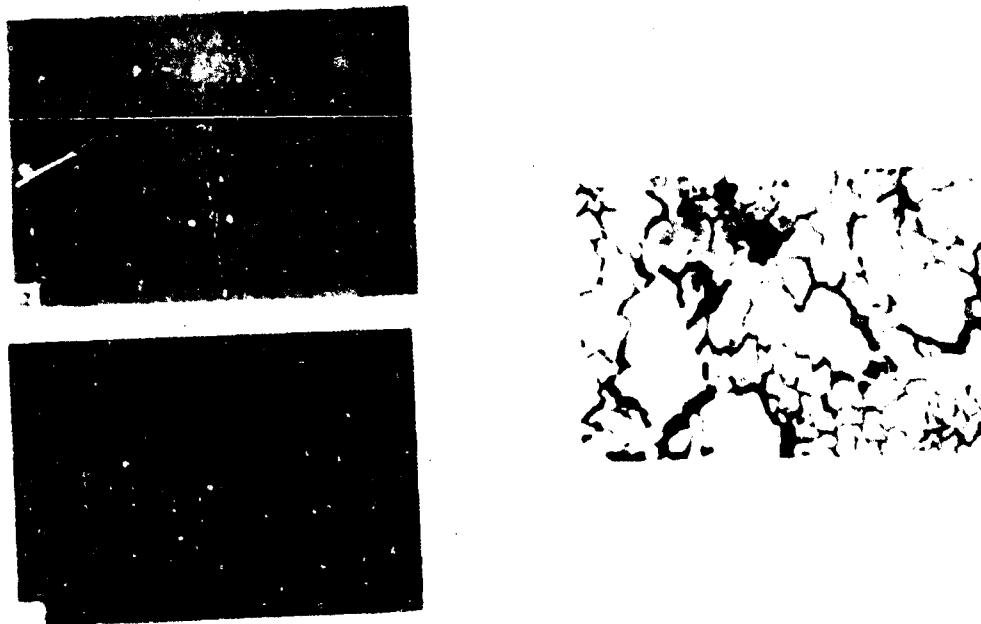
Fig. 1.22. Photographs of Coatings Based on Acrylic Copolymers of Various Hardnesses: a. Butylacrylate; methylacrylate = 40:60; b. Methylacrylate; methylmethacrylate = 70:30; c. Methylcrylate: methylmethacrylate = 60:40.

-44-

Duration, hr.
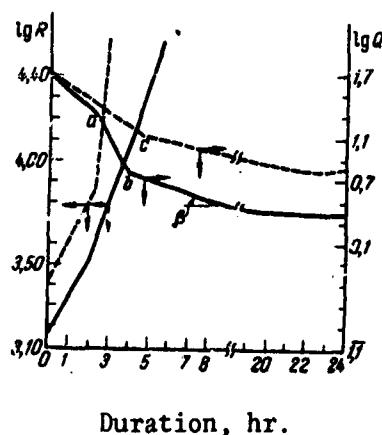
Fig. 1.23. Kinetics of Latex Film Formation Process (change in water content in latex Q and volumetric electrical resistance R) for various copolymers: —————, ethylacrylate with Methylmethacrylate and Methacrylic acid; ----, Ethylacrylate with Methacrylic Acid.

The capillary system is not formed in the case of a latex polymer in the viscous flow state, apparently as a result of the gradual coalescense of the latex particles; due to this, in place of the capillary structure, bodies are formed which consist of blocks of coalesced particles. Therefore, the increase in the rate of the drying process does not occur for this latex at this concentration, although the rate of increase of the electrical resistance does increase.

Influence of Chemical Structure of Polymer on Film-Formation Process

Although certain investigators have stated the opinion that film formation depends more on the colloidal and rheological properties of a latex than on the polymer type [47], recent works dedicated to film formation of latexes have noted an influence of chemical polymer composition on this process. For example, in one work [55], the influence of the hydrophilsolicity (vapor permeability) of the polymer is demonstrated; and in other works [214, 215], the influence of the degree of polarity is pointed out.

Studies of film formation from latexes performed in recent years, considering the degree of branching of macromolecular chains [216,217], their polarity [206] and the content of small quantities of various functional (polar) groups [207], have led to the conclusion that all of these factors influence the kinetics of the process.

A study of the influence of branching of linear macromolecules was performed on a series of specially synthesized (under identical conditions) latexes of copolymers of vinyl acetate and alkylacrylates, differing in the quantity and branching of the alkyl radical -- methylacrylate ($-CH_3$), ethylacrylate ($-CH_2CH_3$), n-butylacrylate ($-CH_2-CH_2-CH_2-CH_3$) and 2-ethylhexylacrylate ($-CH_2$ $-CH-CH_2-CH_2-CH_2CH_3$).

CH_2
CH_3

-45-

The dimensions of particles and the degree of adsorption saturation of their surface were the same for the various latexes. In order to eliminate the influence of the physical state of the polymer, the relationship between the vinylacetate and alkylacrylate were selected so that identical values of modulus of elasticity were achieved for all copolymers . The greatest drying rate was characteristic for the latex of the vinylacetate and methylacrylate copolymer, the slowest drying rate was noted for the copolymer with 2 -ethylhexylacrylate; the copolymers with ethyl-and butylacrylates ocuppied an intermediate position. Coatings of latexes of the copolymers of vinylacetate with methylacrylate were characeterized by the least water adsorption and the greatest transparency. The results produced can be related to the degree of coalescence of the polymer particles, resulting from diffusion prccesses of sectors of macromolecules located on the surfaces; with increasing length and branching of side chains, with the transition from methyl-and ethyl- to n-butyl- and 2-ethylhexylacrylate, diffusion processes become slower. This retards the film-formation process and causes the formation of more brittle latex film structures.

A study [206] of the influence of polarity of the polymer on the rate of film formation using latexes of various copolymers of ethylacrylate as an example showed that the rate increases with increasing polarity of the polymer, but in all cases the process occurs in three stages. In the first stage, when the concentration of latex is 60-70%, the rate of film formation is constant; in the second stage, as the concentration increases to 80%, the rate increases, then in the third stage, as the concentration reaches 91-93%, the rate drops. Data on the rate of occurrence of the third stage of film formation, characterized by tan β (see Fig. 1.23), are presented in table 1.4.

Table 1.4. Rate of last stage of film formation (tanβ) as a function of chemical composition and modulus of elasticity of polymer

Polymer Composition		Modulus of Elasticity at 100% Elongation, kg/cm^2	Tan β
Monomers	Relationship of Monomers, mol		
Ethylacrylate, styrene, methacrylic acid	0.5:0,5:0,018	118.10	0.210
Ethylacrylate, methyl-methacrylate, methacrylic acid	0.5:0,5:0,018	116.87	0.550
Ethylacrylate, vinyl-acetate	0.5:0.5	4.39	0.733
Ethylacrylate, acrylo-nitrile	0.5:0.5	16.62	0.833
Ethylacrylate, acrylo-nitrile, methacrylic acid	0.5:0,5:0,018	61.92	1.333

As we can see from these data, during this stage of the process the rate of film formation depends more on the polarity of the copolymer than on the modulus of elasticity [201].

The functional groups contained in the polymer also influence the film-formation process [218,219]. For example, the introduction of 4-5 mol.% of $-CONH_2$ groups to the composition of the polyalkylacrylate macromolecule sharply decreases water absorption and increases the free film strength, as we can see from the data of [207], presented in table 1.5.

Table 1.5. Dependence of water absorption and strength of free polyalkyl acrylate films of latexes on presence of functional groups in copolymer

Monomers	Composition of Copolymer Relationship of Monomers, mol	Water Absorption After 842 hours, %	Tensile Strength, kg/cm^2
Methylacrylate, butylacrylate	0.73:0.27	133.0	Viscous Flow
Methylacrylate, butylacrylate, methacrylic acid	0.68:0,26:0.06	123.4	7.5
Methylacrylate, butylacrylate, acrylonitrile	0.65:0,26:0,09	94.7	6.8
Methylacrylate, butylacrylate, methacrylic acid amide	0.68:0.26:0.06	11.7	48.7

The introduction of carboxylic or nitrile groups has a significantly weaker effect than amide groups on the properties of the films.

Similar results were produced [207] in a study of the kinetics of film formation from 40% acrylic polymer latexes; the rate of the process was greatest in the case of polymers containing amide groups, and least in the case of polymers containing carboxylic groups. This dependence can be explained on the one hand by the facilitation of diffusion of water through the polymer particles containing hydrophillic groups [55]; however, on the other hand, the increase in the rate of film formation in the stage when the particles come into direct contact may be related to facilitation of their coalescence in the case of polymers containing polar groups which are concentrated on the surface in contact with the aqueous phase (water layers between particles). The presence of polar groups in the macromolecular segments located on this surface might influence the freedom of their rotation, the structure of the films formed and the distribution of emulsifiers in them [207].

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There is some interest in the study of the internal stresses arising in this case for an understanding of the mechanism of the formation of latex coatings on a substrate.

Various methods were used to characterize the process of formation of latex coatings on the substrate: determination of changes in coefficient of reflection of a polarized ultrasonic wave from the boundary between the latex coating and fused quartz, with the results recorded on an oscilloscope [215], polarization-optical measurement of internal stresses in a glass substrate, arising during formation of a coating on its surface, with automatic recording of the results [220].

Duration, hr
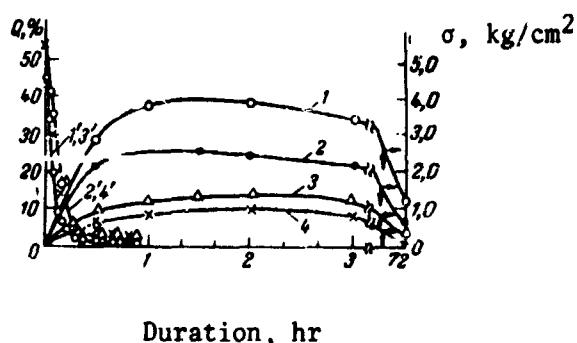
Fig. 1.24. Kinetics of the process of formation of coatings of latexes (Change in water content in latex Q and internal stresses σ) based on various copolymers: 1, 1', methylacrylate, butylacrylate, methacrylic acid; 2,2', methylacrylate, butylacrylate; 3,3', methylacrylate, butylacrylate and methacrylic acid amide; 4, 4', methylacrylate, butylacrylate, acrylonitrile.

The change in internal stresses defined by the polarization optical method with a change in moisture content of acrylic polyer latex films containing various functional groups is shown on Fig. 1.24.

As we can see from Fig. 1.24, all of the latexes studied, when dried on a glass substrate, show at first an increase in internal stresses, apparently resulting from the development and growth of contacts between latex particles, on the one hand, and between them and the substrate on the other hand, followed by a drop corresponding apparently to the occurrence of relaxation processes. It is characteristic in this case to see a significant increase in internal stresses in the last stage of film formation, when the evaporation of water has practically ended. The magnitude of internal stresses does not result from the hydrophillic nature or rigidity of the polymer, but rather correlates with the adhesion bond of the coating, characterized by the limiting critical stresses at the division boundary between film and substrate, leading to spontaneous separation of layers from the substrate, as we can see by comparing Figs. 1.24 and 1.25.

-48-

σ,kg/cm^2
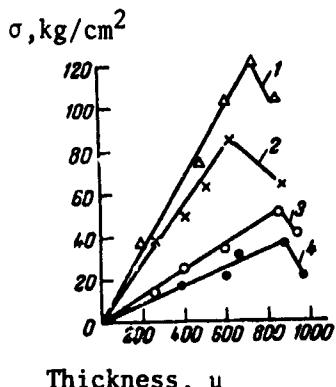
Thickness, μ

Fig. 1.25. Internal stresses as a function of thickness
of epoxy coating applied to latex coatings of various
copolymers: 1. methylacrylate, butylacrylate, methacrylic
acid; 2. methylacrylate, butylacrylate; 3. methylacrylate,
butylacrylate, methacrylic acid amide; 4. methylacrylate,
butylacrylate, acrylonitrile.

The adhesion increases as carboxyllic groups are added to the copolymer
and decreases as amide and nitrile groups are added.

From the kinetic dependences produced, we can conclude that the formation
of the structure of a latex coating, related to the formation of new contacts
and bonds within the coating, occurs with a negligible content of moisture
in the system. The nature of the structure developed is apparently influenced
by the interaction of macromolecular segments on the surface of the polymer
particles and the bonds arising between polar groups on this surface and the
substrate; the relationship of forces of these two interactions apparently
determines the degree of internal stresses.

Influence of Emulsifier on Film-Formation Process

The role of the emulsifier in the latex film formation process was most
thoroughly analyzed by Voyutskiy [222-229]. He believes that in the last
stage of evaporation of water, the most important stage from the standpoint
of technology, the latex film takes on its characteristic structure and pro-
perties. The emulsifier contained in it is dissolved in the polymer or
gradually removed from the surface of the globules and collected in individual
accumulations between them. Sites form on the surface of the globules, un-
coated or almost uncoated with emulsifier, which then serve to join the
polymer globules, which is necessary for formation of a continuous, strong,
water-insoluble film.

The degree of merging of globules depends on the adhesion of the polymer,
the content of emulsifier in the dispersion, its solubility in the polymer
and the conditions under which the coating is formed. With good autohesion
of the polymer and a small quantity of emulsifier, capable of being dissolved

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in the polymer, homogeneous films are formed, not differing significantly
in their properties from films produced from polymer solutions. With less
favorable conditions, a microheterogeneous film is formed, in which the resi-
due of undissolved emulsifier is dispersed in the polymer. Films of this
structure do not transmit water and water vapor if the film former is suf-
ficiently hydrophobic.

When the content of emulsifier is great or it is poorly soluble in the
polymer, the dried film consists of two mutually penetrating networks of
emulsifier and film former. The presence of capillaries filled with the
hydrophillic emulsifier results in the possibility of washing of the emul-
sifier or other water-soluble materials from the polymer. With a very high
quantity of emulsifier insoluble in the polymer, a film is formed in which
the globules of polymer are surrounded by emulsifier on all sides. These
films redisperse in water, have low elasticity and therefore are of no
practical interest. Voyutskiy believes that the films produced from latexes
are almost never characterized by any of the structures described above.
We can only speak of the predominance in the films of microsectors with
structures of one type or the other.

In another work [209], the action of an emulsifier is assumed complex;
by decreasing the interphase tension at the polymer-water boundary, it
influences the dimensions of polymer particles and, consequently, the dimen-
sions of the capillaries. As the particle diameter decreases, capillary
forces increase [55, 215, 229], as the minimum temperature and time of
drying decrease.

It has been suggested [48], that the water absorption of films depends
on their content of salts, not of emulsifier. In certain cases, as is
known, large quantities of emulsifier contained in a latex may be removed
on the surface of the film as it dries; this results in very low water
absorption of the coating [72].

As was shown in [230], the optimal distribution of emulsifier in the
latex film suggested by Voyutskiy is not realized, since the mobility of the
latex polymer, even in the state of viscous flow, is insufficient for this.
Actually, if the polymer particles do not form a sufficiently mobile medium
during coalescence for dissolution of the emulsifier or for its localization
in the form of micelles, it remains between the initial latex particles and
may cause high water absorption of the film. It has been demonstrated [230],
that the mobility necessary for this localization of emulsifier is achieved
in the case of acrylic polymers only when a certain quantity of organic
solvent is introduced to the latex particles, following evaporation of the
water. In this case, homogeneous films are formed, which practically do not
swell in water if the polymer is hard enough.

A similar effect is observed in the formation of films of aqueous
emulsions of nitrocellulose solutions, when the water absorption of the
films produced from these emulsions and their organic solutions containing
the same quantity of emulsifier practically do not differ [231]. However,
the water absorption of films made of latexes containing significant

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quantities of emulsifier is frequently an order of magnitude higher [165]. It also follows from this that even with a very low content of emulsifier in the latex film, its water absorption depends on the structure of the film.

It should be noted that the localization of the emulsifier in itself does not assure high water resistance of the film containing it; this requires also sufficient packing density of macromolecules. Thus, experiments which we performed [67, 232] have shown high water absorption of elastic films produced from solutions of latex polymers in organic solvents, i. e., under conditions of distribution of the emulsifier in the energetically most suitable manner. The water absorption of films of acrylic latexes synthesized with identical consumption of initiator and emulsifier, is decreased with increasing modulus of elasticity of the polymer and increasing molecular weight [165]. This can be explained by an increase in intermolecular interaction [233], causing a decrease in the number of "holes" responsible for water absorption, formed by thermal movement of the polymer macromolecules. A similar dependence of water absorption of latex films made of polyvinyl acetate and its copolymers with butylacrylate on deformation resistance of the polymer has been produced [234].

Influence of Structure of Latex Particles on Film-Forming Process

In works on the mechanism of film formation of latexes, the latex particle has been assumed as the structural element of the latex film [48, 55, 195-205]. The process of film formation has been looked upon as flocculation of latex particles with their subsequent deformation under the influence of the developing capillary forces [235-237]. Studies of the film structure of styrene and rigid bivinyl-styrene latexes have seemed to confirm this opinion [238-242]. In some works, proof of hexagonal packing of latex particles is presented, which can prove their deformation during the process of film formation [200, 237, 243]. In other works, it is assumed that if the polymer particles are sufficiently plastic, they coalesce with some surface interpenetration [235, 236, 244]. In all these works, the latex particle itself is looked upon as the primary aggregate of the disordered, interwoven macromolecules, held together by the intermolecular interaction forces.

Up to now, the study of the fine structure of latex coatings and its influence on the properties of the coatings have not been given sufficient attention. The study of the latex particles has consisted primarily of determination of their dimensions, the study of film structures has consisted of observation of replicas taken from the film surface under the electron microscope.

However, certain authors believe that the particles of latex rubber are formed as a result of combination of primary spherical globules of ultramicroscopic size, the difference between the structure of the internal portion of the latex particle and its perpherial portion consisting in the varying degree of aggregation of the primary globules [245-247].

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Studies of film formation of industrial synthetic rubber latexes have also stated the opinion that the globules of latexes and latex coatings are supermolecular structures [65]. Depending on the nature of the functional groups contained in the polymer even in small quantities, latex films may differ significantly in various properties.[207].

For example, when 4-5 mol.% hydrophillic carboxyl groups was introduced, a decrease in the water absorption of a film and an increase in its strength were observed, while when the same quantity of ¬mide groups was observed, the same dependence was expressed much more sharply -- the strength increased by more than 5 times, water absorption was decreased from 140 to 11%. The latex particles and the film produced of them are characterized by a definite structure[1], differing in nature depending on the chemical nature of the functional groups contained in the macromolecules. For example, the particles of polyalkylacrylate latex and its copolymer with methacrylic acid have a globular structure (Fig. 126a), while the copolymer with methacrylic acid amide shows a fibrillar orientation of the polymer in the globules (Fig. 1.26b). Since the latex was produced under the same polymerization conditions, these studies have shown that the supermolecular structure of the latex particles may differ, depending on the nature of the functional groups contained in the polymer in small quantities.

Studies of the structure of latex films of the same copolymers using a similar method, confirmed the globular nature of the structure for latex films of polyalkylacrylate polymer and its copolymer with methacrylic acid (Fig. 127a) and the fibrillar nature of the structure for the copolymer with methacrylic acid amide (Fig. 127b)
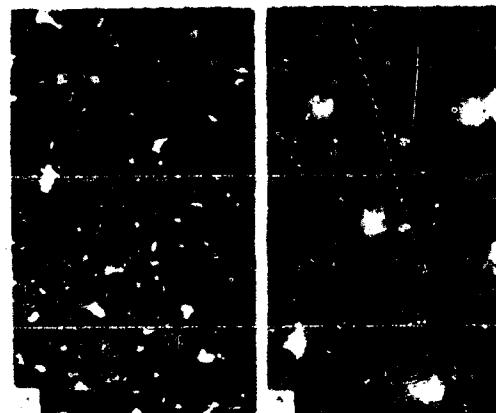
Fig. 1. 26. Electron microscope photographs of latex particles of polyalkyl acrylate copolymers (25,000 ×): a. methacrylic acid amide b. methacrylic acid.

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[1] The internal structure of the particles of latexes and films was determined by the method of low-temperature etching of specimens with active oxygen, which was produced in an electrodeless high-frequency discharge [66,248].

The structure of films made of the copolymer of polyalkylacrylate with methacrylic acid and methacrylic acid amide produced from solutions shows considerable damage, as can be seen from electron microscope photographs of the films (Fig. 1.27c and d).

A comparison of the physical-chemical properties of latex films and films produced of solutions of the same polymers has shown that they differ significantly. The mechanical properties of latex and solution films, as characterized by stress-strain curves, are shown on Fig. 1.28. This figure shows that the latex films have significantly higher tensile strength and elasticity than the film produced from solutions of the same copolymers.

Thus, the structure of latex films, distinguished by the nature of the functional groups contained in the polymer in small quantities, shows a sharp difference. The fibrillar orientation of the polymer, as has been shown for the copolymer containing amide groups, causes a sharp increase in strength and a decrease in water absorption of latex films. This is explained as follows: in the latex film, these groups are located in a more oriented manner than in the solution film, i. e., they are located on the surface of the latex particles, which leads to formation of a more ordered structure due to the greater realization of interactions by hydrophillic groups capable of forming hydrogen bonds
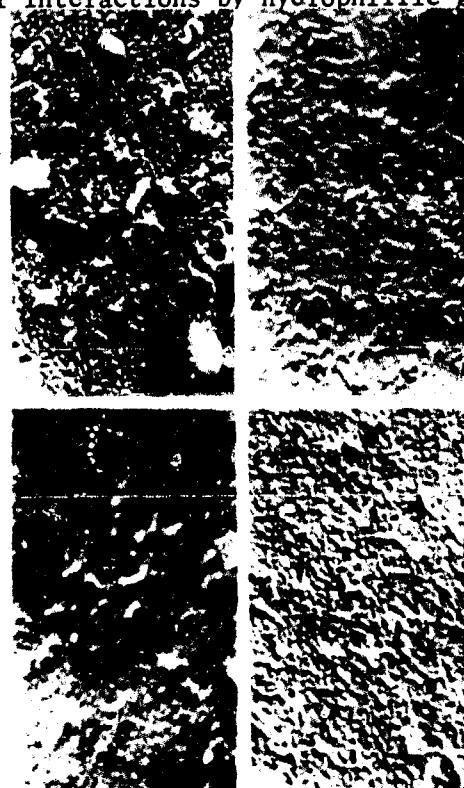
Fig. 1.27. Electron microscope photographs of films; a. latex copolymer of polyacrylate with methacrylic acid; b. latex copolymer of polyacrylate with methacrylic acid amide; c. solution of copolymer of polyacrylate with methacrylic acid; d. solution of copolymer of polyacrylate with methacrylic acid amide.
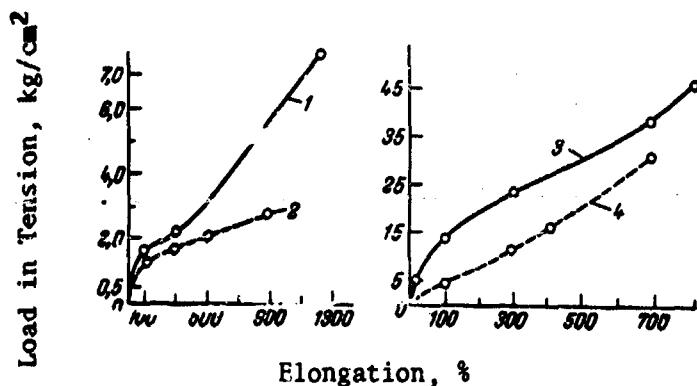
Fig. 1.28. Stress-strain curves for films produced from:
1. latex of copolymer of polyalkylacrylate with methacrylic
acid; 2. solution of copolymer of polyalkylacrylate with
methacrylic acid; 3. latex of copolymer of polyacrylate
with methacrylic acid amide; 4. solution of copolymer of
polyacrylate with methacrylic acid amide.
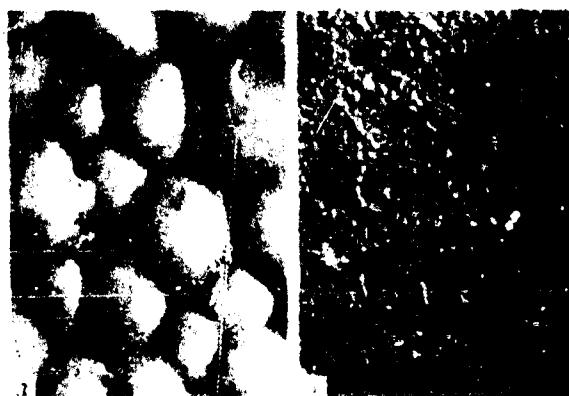
Fig. 1.29. Electron Microscope Photographs of Films of Polyvinyl-
acetate latexes dried at various temperatures (following oxygen
etching) a, 20°C; b, 130°C.

The presence of the homogeneous structure also increases film strength
in comparison with structures having noncoalescing globules. This can be
clearly seen on the example of the polyvinyl acetate latex. Films produced
at room temperature are characterized by the presence of noncoalescing
globules (Fig. 1.29a), while those produced at 130°C have a homogeneous
structure (Fig. 1.29b); the tensile strength and water absorption of the
film are significantly changed in this case, as we can see from the data
presented below:

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Drying temperature	20°C	130°C
Tensile strength, kg/cm^2	17	27-30
Water absorption, %	24	6-7

The descriptions of film formation from latexes which we have presented show that it must be studied not only from the point of view of the physical and chemical processes of evaporation of water, merging of latex particles and distribution of emulsifier, but also considering structural conversions occurring in the process of formation of latex films and coatings, related to the chemical structure of the polymer, influencing the morphology of the particles and particularly of their peripheral sectors.

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CHAPTER II

FILM FORMATION DURING POLYMERIZATION OF MONOMERS IN THIN LAYERS

When coatings are produced directly from monomers by radical polymerization, the film-forming process is significantly simplified. The first works in this area have yielded promising results [1-9].

Mechanism of initiation and polymerization

The mechanism of polymerization of monomers in thin layer directly on the substrate was not studied until recently, although the kinetics of polymerization of oligomers in thin layers were studied in a number of works [10-15]. We know that these two processes differ significantly from each other due to the lower viscosity and greater volatility of monomers in comparison with oligomers, which are low-molecular polymers. Furthermore, in the case of polymerization of monomers, the influence of the oxygen in the air, which easily penetrates the reaction system, is greater [16,17].

Influence of oxygen in the air on the polymerization process

It is known that the process of radical polymerization is inhibited or initiated in the presence of molecular oxygen, depending on the concentration of the oxygen in the reaction system [16].

The inhibiting effect of oxygen during polymerization of monomers in a thin layer results from its high concentration in the polymerization system as a result of the great contact surface of the oxygen with this system and the ease of its penetration into the reaction zone. The rate of radical polymerization and the induction period depend on the concentration of oxygen [18-20], which, in turn, is determined by the depth of the layer below the surface, the viscosity of the polymerizing system and its degree of structuring.

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It is assumed [21] that the following reactions occur during the period of oxygen inhibition of radical polymerization:

Development of oxydation chains

$$R\cdot + O_2 \xrightarrow{k_1} RO_2\cdot$$

$$RO_2\cdot + M \xrightarrow{k_2} R\cdot$$
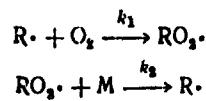
Growth of polymer chain

$$R\cdot + M \xrightarrow{k_3} R\cdot$$

Separation of the chain

$$RO_2\cdot + RO_2\cdot \longrightarrow \quad \text{inactive products.}$$
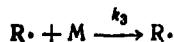
Since $k_3/k_1 < 3\cdot 10^{-5}$ at 50°C, practically all polymer radicals $R\cdot$ will react with oxygen, not with the monomer, although the concentration of the monomer is approximately 10^4 times higher than the concentration of oxygen (solubility of oxygen in methymathacrylate saturated with air 10^{-3} mol/l). Since the reactivity of $RO_2\cdot$ for the monomer is much less than $R\cdot$, the conversion of $R\cdot$ to $RO_2\cdot$ is equivalent to breaking of the chain.

The study of the inhibiting influence of oxygen on the polymerization of methacrylic and acrylic acid esters has shown that the result is a slowing of the reaction of polymer formation and appearance of an induction period [22, 23]. During inhibition, retarded copolymerization of the monomer with oxygen occurs, as the polymer peroxide is formed [24-27]. The peroxide radicals are inactive in the reaction of chain growth, leading to a sharp reduction in the length of the polymer peroxide chains.

The inhibiting influence of oxygen can be significantly decreased by adding reducing agents, particularly tertiary amines, which bind molecular oxygen [20]. The role of the reducing agents is not limited to this: the oxydation-reduction reactions occurring between them and the oxygen can cause polymerization.

It has been demonstrated that in the case of polymerization of oligoester acrylates, the oxidative destruction processes in the induction period are accompanied by polymerization [28], the product of which is the β-polymer (a soluble, more or less branched unsaturated polymer, capable of forming a reticular structure). It is believed that in the presence of the oxygen of the air, the formation of the β-polymer is a necessary stage [15]. Its formation results in an increase in the viscosity of the system, which hinders diffusion of oxygen in the coating. In connection with this, the influx of oxygen is decreased and at some moment conditions are created under which the concentration of oxygen becomes so slight that the oxygen ceases to act as an inhibitor of polymerization. The acceleration of polymerization in this case results not only from the hindrance of diffusion of oxygen into the film, but also from the transition of the reaction between oxygen and the growing polymer chains in the diffusion area [29].

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The inhibiting effect of oxygen on the polymerization process, observed at low concentrations, has been thoroughly studied [7,16,30-32].

It was assumed earlier [30-33], that the initiating effect of oxygen results from the decomposition of perioxides and hydroperoxides formed by interaction of the monomers with oxygen.

Further investigations [34,35] have shown that monomer peroxides are not formed, and that most monomers combine with oxygen to produce copolymers with strict alternation of molecules of the monomer M and oxygen (polymer perioxides): $\cdots M-OO-(-M-OO)_n-M-OO-\cdots$.

The decomposition of this sort of compound initiates the process of polymerization. Thus, in studying the kinetics of polymerization of methyl-methacrylate, initiated by azobutyromitrile in the presence of the oxygen of the air at 50°C, it was determined [21],[31], [32] that a low molecular polymer with a decomposition temperature of about 40°C was formed during the inhibition period.

Agreement has been observed [31] between the processes of polymer formation and decomposition of polymer peroxides in methylmethacrylate: whereas thermal polymerization practically does not occur without oxygen even at temperatures of 100°C, negligible quantities of oxygen immediately cause the reaction. At temperatures of over 100°C, methylmethacrylate is rapidly polymerized, even without other initiators, although the polymer does not contain peroxides and has high molecular weight [36]. In this case, the catalytic effect of the oxygen lies in the formation first of a low molecular copolymer of O_2 with methylmethacrylate (polyperoxide), which is fully decomposed at high temperatures, forming radicals which initiate polymerization. The polymer peroxides of other monomers also have initiating ability [24, 25, 37].

Influence of method of initiation on process of polymerization

In practice, the polymerization of monomers in a thin layer can be initiated by all known methods. During chemical initiation, preference must be given to oxidation-reduction systems.

Chemical initiation. During chemical initiation by oxidation-reduction systems, oxidation-reduction reactions occur between the components of the reaction system directly through the stage of free radicals or through inter-mediate unstable products, which dissociate into free radicals at low tempera-tures. The radicals formed are attached to the double bonds of the monomers and cause polymerization.

One distinguishing feature of oxidation-reduction initiation is the low activation energy, amounting to 10-15 kcal/mol (41.8-62.7 kj/mol). This allows polymerization to be performed at high rates at low temperatures,

sometimes near 0°C, which is particularly important for polymerization in a thin layer[1].

The rate of polymerization initiated by oxidation-reduction systems can be increased by adding soluble metal salts. The ions of the metals, interacting with the peroxides or hydroperoxides, accelerating their decomposition, increase the concentration of free radicals [39, 40). It has been demonstrated [41-43] that oxidation-reduction systems, consisting of a hydroperoxide and a small quantity of a hydrocarbon-soluble salt of a metal of variable valence, can function as reversible systems without introduction of a reducing agent. In this case, the decomposition of the hydroperoxide occurs in a closed cycle, in which the hydroperoxide acts as the oxidizer and reducer. These systems are well regulated, effective sources of free radicals over a broad temperature range, which has resulted in their wide usage in copolymerization of unsaturated polyesters with various monomers [44-46].

It has been shown [47, 48] that oxidation-reduction systems, in the presence of hydrocarbon-soluble salts of variable valence metals can be successfully used for initiation of the polymerization of polyester acrylates in a thin layer. In this case, systems consisting of benzoylperoxide and cobalt naphthenate, cumene hydroperoxide and cobalt naphthenate and others were studied.

According to the experimental data [48], the optimal polymerization mode of polyester acrylates in a thin layer is observed in the presence of benzoylperoxide in combination with cobalt linoleate.

The use of an accelerator (soluble metal salt) together with an initiator (peroxide) simply decreases, without eliminating, the inhibiting influence of the oxygen of the air. This is indicated by the increase in the rate of polymerization with the same initiating systems in an atmosphere of an inert gas.

Active oxidation-reduction systems develop when benzoyl peroxide interacts with various amines. The decomposition of the benzoyl peroxide in the solution leads to formation of benzoic acid and o-benzoyl-N, N'-diphrenil hydroxilimene [49].

More detailed investigations [50-53] of the mechanism of interaction of benzoylperoxide with amines have shown that first, formation of a complex of the amine with the peroxide occurs [53], in which transition of an electron from the amine to the peroxide later occurs, forming iron pairs and the benzoate radical, which is the initiating agent [52,54].

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[1] In contrast to oxidation-reduction initiation, the composition of benzoyl peroxide or azoisobutyric acid dinitrile requires an activation energy of approximately 30 kcal/mol (125 kj/mol), and polymerization with these initiators does not occur below 40-50°C.

Photochemical initiation [38] occurs when ultraviolet radiation is present, with energy sufficient for homolytic breaking of the chemical bond. The radicals causing the reaction arise either as a result of the primary event of dissociation of molecules, or as a result of secondary processes. Regardless of the energy of the radiation used, polymerization always occurs by the radical mechanism at temperatures above freezing.

The kinetics of the reactions of photopolymerization represent no exception to the general kinetic regularities of radical polymerization, but have certain pecularities, resulting from the mechanism of initiation. Excitation of a molecule by light eliminates the necessity of thermal activation. The processes occurring under the influence of radiation are as if without activation, the energy of the initiation reaction is practically equal to 0, and the rate of photoinitiation depends only on the intensity of illumination, not on temperature.

One of the most significant pecularities of this type of initiation results from the selective nature of absorption: light is absorbed only when the frequency of its oscillations corresponds to the absorption band of the monomer molecules.

Photopolymerization is retarded in the presence of oxygen of the air, since the free radicals react with the oxygen of the air more rapidly than with the monomer molecules. The peroxide compounds formed may begin the reaction chain following their decomposition. However, in the overwhelming majority of cases, the temperature must be increased to cause decomposition of the peroxide compounds.

Radiation initiation occurs when ionizing radiation is present, converting the monomer molecule to the excited state. At positive temperatures, polymerization always occurs by the radical mechanism.

In contrast to photochemical processes, ionizing radiation is absorbed by all materials regardless of their chemical structure. The quantity of absorbed energy is approximately proportional to the number of electrons per unit volume of material. At the same time, the number of radicals formed per unit energy expended does not depend directly on the number of electrons per unit volume, but is rather determined by the nature of the material and the medium. This results from the fact that, in addition to the formation of radicals from the excited molecule, these molecules are deactivated, as a result of which the excitation energy is converted to thermal energy. The relationship between these two competing processes determines the yield of radicals.

During radiation, the nature of the initiators added have a strong influence on the rate of polymerization [55]. For example, the polymerization rate of styrene is increased by a factor of 3 if 0.01 mol/l benzoylperoxide is added to the monomer.

-67-

Initiation by the effects of a glow discharge [56-62] is produced by applying a stream of nonaccelerated electrons to a vapor-phase or gaseous monomer, placed in a high voltage electric field. The free radicals and ions form, which receive considerable energy from the electric field applied, initiate the polymerization reaction. The mechanism of this process has not yet been studied.

This method can be used to initiate the reaction of polymerization and copolymerization of styrene, butadiene, ethylene, propylene, acrylates, as well as a number of carbon-containing compounds, which are not polymerized in the presence of other initiators.

It has been established that acrylates are polymerized more slowly than styrene.

Influence of Properties and Structure of Monomer on polymerization Process

The production of coatings directly from monomers is practically expedient only if the losses of monomer during the process of polymerization are practically eliminated. However, since all monomers have significant volatility, special conditions must be created for their polymerization in a thin layer in air.

The main factors determining the film-forming ability of monomers in the initial stages of polymerization, when losses due to evaporation are particularly great, include those which increased the rate of polymerization and reduce the induction period. Therefore, in addition to the reactivity of the monomers, the viscosity and number of double bonds in their molecules, allowing the development of a three-dimensional structure, are also significant, as well as the presence of groups capable of taking part in initiation. Examples of such groups include the tertiary amino groups in aminoalkyl methacrylates [63], the mechanism of chemically initiated polymerization of which has been studied in some detail [64].

The thermometric method has been suggested for the study of the mechanism of polymerization, based on measurement of the rate of heat liberation in a reacting system [65-69].

At the beginning of the process of polymerization of monomers with low conversion, autoacceleration of the process occurs, followed by self-inhibition so that a limiting value of conversion is reached, depending on the type of monomer and experimental temperature. As the temperature increases, the induction period is decreased and the rate of polymerization increased for all monomers. This is clearly illustrated by the kinetic data from the polymerization reaction for various monomers shown in table 2.1.

Table 2.1. Kinetics of polymerization of various monomers with initiation by azoisobutyric acid dinitrile

Monomers	Reaction Temperature, °C	Induction Period, min.	Reaction Rate, kcal/mol·sec (kj/mol·sec)
β-(N-Piperidyl)-ethyl-methacrylate	56,0	9	1,4 (5,8)
	62,5	6	2,5 (10,4)
	71,5	3	5,1 (21,3)
	66,7	18	0,6 (2,7)
β-diethyl aminoethyl methacrylate	71,0	1:	1,1 (4,7)
	75,4	8	1,4 (5,8)
	70,0	58	0,7 (3,1)
	76,5	41	1,3 (5,4)
n-octylmethacrylate	78,0	35	,6 (6,7)

As we can see from table 2.1, when initiation is performed by azoisobutyric acid dinitrile, β-(N-piperidyl)-ethyl-methacrylate is most activily polymerized, followed by β-diethyl aminoethyl methacrylate and, finally, n-octylmethacrylate. Polymerization of aminoalkyl methacrylates, in comparison with n-octylmethacrylate, is characterized by a shorter induction period and deeper conversion in an equal length of time. The greater activity of aminoalkyl methacrylates in comparison with n-octylmethacrylate during polymerization can be explained by the presence of the tertiary amino group.

β-(N-piperidyl)-ethyl-methacrylate is polymerized in a thin layer in air by initiation with perioxides as well.

The main factors influencing the rate of film formation from monomers include the activation energy of the process and the viscosity of the polymerizing system.

A reduction in activation energy can be achieved by selecting the corresponding initiators, which are active in the presence of the oxygen of the air. The values of activation energy are presented below for the case of polymerization of β-(N-piperidyl)-ethyl methacrylate in the presence of various initiators:

Initiator	Activation Energy, kcal/mol (kj/mol)
Aziosobutyric acid dinitrile	19.6 (81.7)
Tertiary butylperoxide	10.2 (42.5)
Benzoylperoxide	9.0 (37.6)

Initiation with azo-compounds does not decrease the activation energy [79-81]; therefore, polymerization in the presence of these initiators should be performed only at a temperature over 50°C. When initiation is performed with peroxide, the activation energy is decreased to 9-10 kcal/mol (37.6-41.8 j/mol), which indicates the oxidation-reduction mechanism of initiation; polymerization of aminoalkyl methacrylates with benzoylperioxide and tertiary butylperoxide is observed at temperatures below the temperature of thermal decomposition of these peroxides.

In spite of the low values of activation energy, the induction period during polymerization of aminoalkyl methacrylates is long. This results from the increased inhibiting influence of the oxygen of the air during polymerization in a thin layer. Performance of the polymerization process at temperatures near room temperature is possible by a combination of oxidation-reduction initiation with increased viscosity of the system as a result of structuring, allowing the access of oxygen to the polymer layer to be limited.

Influence of Substrate Material on Polymerization Process

In the case of production of polymerization coatings in a thin layer, it is necessary to consider the possibility of essential inhibition or initiation by the substrate material [15]. For example, glass and aluminum are rather passive and have practically no influence on the rate of polymerization. Iron, however, can increase the rate of radical chain decomposition of initiators such as hydroperoxides and thereby accelerate the polymerization process.

Kinetic studies have shown [63] that when aminoalkyl methacrylates are polymerized in the presence of copper, the activation energy of polymerization is decreased, as we can see from the data presented in table 2.2 for the case of polymerization of β-(N-piperidyl)-ethyl-methacrylate.

Table 2.2. Values of Activation Energy for Polymerization of β-(N-piperidyl)-ethyl-methacrylate.

Initiator	Substrate Material	Activation Energy, kcal/mol (kj/mol)
Aziosobutyric acid dinitrile	Aluminum	19.6 (81.7)
Without initiator	Copper	14.5 (60.5)
Aziosobutyric acid dinitrile	"	13.9 (58.0)

Furthermore, the induction period is reduced and the degree of conversion of monomers is increased. According to the data of other authors [15], copper inhibits the polymerization process strongly.

Formation of Coatings from Monomers

The production of coatings by polymerization of monomers directly on the surface of products is considered one of the most pressing problems in the technology of the paint and varnish industry. The methods of production of coatings differ depending on the method of initiation of polymerization in the thin layer. The following methods of production of coatings are of commericial significance: in the field of an electrical glow discharge [82-85] and under the influence of ionizing radiation [86,87]. The use of these methods is possible only for painting of small products of constant profile and requires

relatively complex apparatus. Furthermore, a method has been developed for the production of coatings by the action of ultraviolet radiation.

The performance of the process of film formation from monomers by chemical initiation in air excludes the use of complex technological equipment, making this method more economical than the first two.

+

Vacuum

Monomer vapers

Heat transfer medium
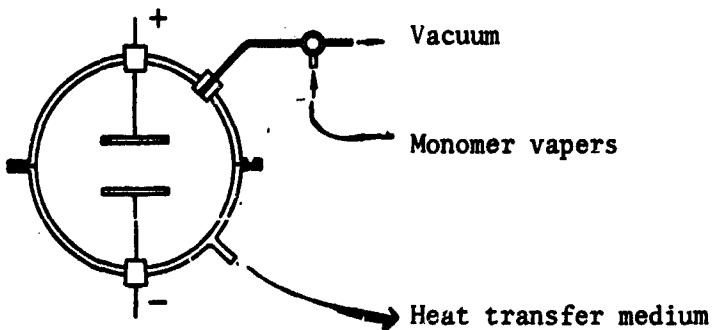
Fig. 2.1. Diagram of an Installation for Production of Coatings in the Field of an Electrical Glow Discharge.

Production of Coatings in the Field of an Electrical Glow Discharge

This method of production of polymer coatings was first suggested by Coleman [88]. The products to be coated is placed in a sealed chamber (Fig. 2.1), behind the cathode; a vacuum of 10^{-2}-10^{-3} mm Hg is then created in the chamber and vapors of the monomer admitted. Then a voltage of 300-650 v is applied to the electrodes, and the glow discharge which then occurs causes the formation of a nonporous polymer coating of homogeneous thickness.

The thickness of the layer depends on the properties of the monomer, its vapor pressure, current density, chamber size and distance between electrodes [88-93].

The optimal vapor pressure of the monomers is determined on the basis of the fact that ionization occurs best of all at minimal pressure; however, the coatings produced at minimal pressure are too thin. Films of greater thickness are formed at higher pressures, but then a large quantity of the monomer is polymerized in the space between electrodes, resulting in great monomer losses. This method can best be used for the production of coatings 0.1-5µ thick. However, some investigators have produced coatings of 25µ and thicker [94,95].

The mechanical properties of the coatings depend on the electrode temperature: harder coatings are produced at higher temperatures.

The production of pigmented coatings by this method is practically impossible.

In the USA, an installation has been developed [91] for the production of polymer coatings 0.1-1µ thick on the surfaces of conductors, semiconductors

and insulators. The product coated in this case is placed behind a perforated sheet cathode.

Other installations are also known for the production of monomer coatings under the influence of a glow discharge [92,93]. In one of these installations, the polymer coatings 1µ thick are produced on a steel strip moving at 0.5 m/sec, while another produces coatings on steel sheets.

An apparatus has also been described [84] in which the formation of the coating occurs on the bent surface of a steel drum clamped in a teflon holder. The monomer is evaporated from a boat beneath the drum at 10^{-2} mm Hg and, following deposition, is subjected to ion bombardment, initiated and maintained by a glow discharge in an atmosphere of argon. The properties of the coatings produced in this case are adjusted by the discharge current and the rate of evaporation. Coatings have been produced by this method up to 10µ in thickness.

The method of application of thin coatings in the field of an electric alternating current glow discharge is also beginning to be developed in the Soviet Union [96-98].

This method is used to produce homogeneous coatings having high adhesion, good electric insulating properties, which are retained even after repeated cyclical testing at temperatures between +20°C and -173°C, and which are resistant to the effects of high temperatures and chemical reagents. However, when stored in air, the coatings absorb oxygen, which probably results from the presence of free radicals in the polymer, which are subject to peroxide oxidation [92].

The use of this method allows significant reductions in the area of shops, automation of production and elimination of drying devices, although the necessity of creating a deep vacuum in the reaction chamber limits the popularity of this method in industry to some extent.

Production of Coatings by the Effects of Ionizing Radiation

In this method, polymerization of paint and varnish systems (monomers with pigments and fillers) following application of the material to the product by methods of airless sputtering or flooding occurs practically instantaneously. The product is most frequently placed on a conveyer, which moves beneath a beam of high or low energy electrons.

The maximum depth of penetration of the electrons into the product depends on the density of the mass of the product and the energy of the electrons. This method can be used to treat products from 0.25 to 3 mm thick, using paint and varnish compositions based on polyester and other resins, containing unsaturated monomers [99,100]. In the presence of the oxygen of the air at room temperature with reduced radiation doses, coatings 12.5 to 3,000µ thick can be produced.

In England, an experimental installation has been used for radiation hardening of coatings, in which the source of high energy electrons is the tungsten cathode of an electron gun operating at 125-130 kv. The current of the beam is 200 ma for each 25 mm width of the polymerized coating. The products are moved through a vacuum chamber in which a pressure of 10^{-5} mm Hg is maintained at a speed of 60 m/min. The beam of electrons is directed toward the coating being polymerized through a slit made of aluminum foil. The hardening time is a few seconds [101].

A radiation curing installation has been constructed in the USA [102] (Fig. 2.2) with a productivity of 1115 m^2/Hr, using a radiation dose of 2 Mrad. The accelerating head in this installation is separated from the power supply and requires minimum screening -- 12.7 mm of lead. The high voltage is fed through a cable to an insulated SF_6 head and excites a thoriated tungsten filament. The filament transmits a stream of electrons focused by a lens and accelerated to 300 kv in an evacuated CRT. The beam is deflected by a magnet and passes through a slit 0.025 mm wide. The operational expenses of this installation are one third those of an ordinary drying oven, the capital cost is the same.
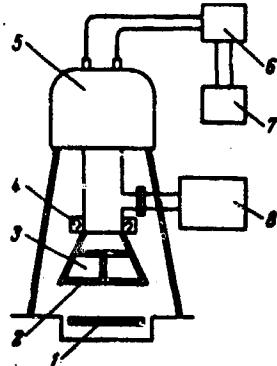
Fig. 2.2. Diagram of Installation for Production of Coatings by Radiation Initiation: 1. Rolled Product Transporter; 2. Thin Shielded Window; 3. Radiation Funnel; 4. Magnet; 5. Electron Gun Generator; 6. Vacuum System; 7. Control Panel; 8. High Voltage Installation.

Curing by means of a high energy beam of electrons is uneconomical due to the useless expenditure of energy, the high capital investments and servicing costs, the necessity of placing products in a vacuum and the damage to substrates resulting from heating. Furthermore, a high energy electron beam contains other dangerous types of radiation, from which it is difficult to protect workers in a production situation [103]. Therefore, it is more expedient to cure coatings using low energy electrons. This simplifies the design of installations, since the beam of low energy electrons causes polymerization in the presence of air at atmospheric pressure. The use of a low energy electron beam is recommended for polyester-base paint and varnish materials, since materials based on methacrylates, vinyl esters, olefins, acetylenes and unsaturated oils are insensitive to curing by an electron beam at radiation-doses

which are considered economical [104]. The addition of other polymerization initiators (for example peroxides) does not accelerate electron beam curing.

Coatings produced by this method are resistant to the effects of solvents, resulting from the formation of reticular polymer under the influence of the electron beam.

The mechanical properties of coatings produced by radiation curing do not differ from the properties of coatings cured in the presence of peroxide initiators at high temperature.

The use of this method with a low energy electron beam allows us to increase the curing rate, decrease capital investments, reduce the consumption of electric power, and also produce coatings on substrates such as wood, cardboard and plastics [99], [103]. The primary limitation for the application of the method of radiation curing in industry is the shape of the products coated. At the present time, this method is used for curing of coatings on products of simple shape only.

Production of Coatings by the Action of Ultraviolet and Infrared Radiation

With this method, the paint and varnish material, most frequently a mixture of unsaturated polyester resin with vinylic monomer [105-107], is applied to the product to be painted by pouring (expending 150-200 g/m^2), then polymerized by irradiation for several minutes with an ultraviolet lamp at a distance of 15-20 cm.

The Bayer Company has developed a photopolymerizing unsaturated polyester, produced as a 65% solution in styrene [107]. This polyester is designed for the production of transparent or semitransparent single-component coatings on wood. Curing is performed under the influence of ultraviolet radiation with a wave length of 300-400 μ with no organic peroxides in a process lasting 20 minutes. Pigmented coatings based on the polyester cannot be cured by this method, since the rays do not penetrate to the required depth in the coating. The maximum layer thickness at which the coating will be fully cured depends on the absorption of ultraviolet light by the components of the coating.

Coatings cured by ultraviolet radiation have high adhesion and high protective properties [107, 108].

Curing by infrared radiation is also significant for the technology of paint and varnish coatings. Fig. 2.3 shows a diagram of an installation for the production of polymer coatings using infrared rays. The prepolymerizer 1 performs preliminary polymerization of the monomer or monomer mixture to a liquid prepolymer, which is then fed into mixer 2, where the catalyst is added. The prepolymer is fed from vessel 3 through a funnel-shaped slit onto a substrate. The thickness of the layer is adjusted by calibrating rollers 4. The curing of the coating begins in the polymerization chamber under the influence of infrared radiation, while final polymerization occurs in a chamber of hot air.

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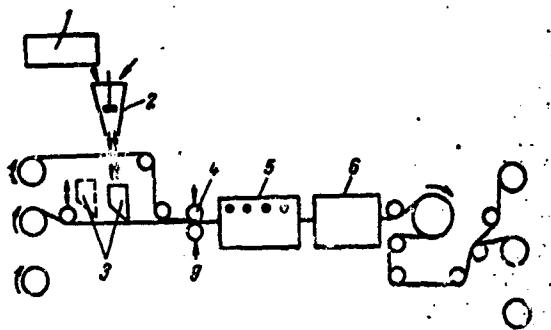
Fig. 2.3. Diagram of Installation for Production of
Coatings Using Infrared Radiation: 1. Prepolymerizer;
2. Mixer; 3. Vessel for Transmission of Prepolymer
to Substrate; 4. Calibrating Rollers; 5. Infrared
Curing Chamber; 6. Final Curing Chamber.

The use of this method allows the expenditure of labor for servicing to
be decreased by 50%, while decreasing the duration of the curing process by
approximately 5 times in comparison with ordinary high temperature drying.

Production of Coatings by the Action of Oxidation-Reduction Initiators

With this method, polymerization is initiated by the action of oxidation-
reduction initiators; therefore, in contrast to the methods of initiation
described above, no special apparatus is required. The difficulty involved
in the performance of this method is the inhibiting effects of oxygen, the
contact surface of which with the monomer is quite great. Furthermore,
evaporation of the monomer may lead the process of polymerization. This can
be prevented by accelerating the polymerization process, since as the first
quantities of polymer appear, the vapor pressure of the monomer over the
polymerizing system is decreased, thus decreasing the losses of monomer due
to evaporation.

The role of viscosity during thin layer polymerization in the presence
of the oxygen of the air is particularly important, since, in addition to
its influence on the molecular-kinetic behavior of the polymerizing system,
it determines the rate of penetration of oxygen into the depth of the coating.

The inhibiting influence of oxygen during polymerization in a thin layer
can be significantly decreased by structuring the system, which can be achieved
by chemical and physical-chemical methods (addition of polyfunctional copoly-
merizing monomer or active filler, causing the formation of a thixotropic
system).

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Structuring of the system of aminoalkyl acrylates is performed using triethanolamine trimethacrylate. Experiments have shown that the addition of this comonomer in certain quantities to the basic monomer, β-(N-piperidyl)-ethy-methacrylate, decreases the inhibiting influence of the oxygen of the air [63], [109]. The effect observed is apparently related to an increase in viscosity of the system as a result of formation of a 3-dimensional structure at the beginning of polymerization[1]. Therefore, the introduction of triethanolamine trimethacrylate has a positive influence primarily following the beginning of polymerization of the β-(N-piperidyl)-ethyl-methacrylate in the presence of benzoil peroxide, but has little influence on the induction period, as can be seen from the data presented below:

Concentration of triethanolamine trimethacrylate,%	Polymerization Temperature, °C	Induction Period, min
0	36	19
5	36	15
0	43	14
5	43	11

The introduction of an active filler such as acetylene black with a surface of 99 m^2/g, has a great influence on the polymerization process of aminoalkyl methacrylate in a thin layer in air. As experiments have shown, the introduction of black decreases the induction period of polymerization.

The effects of black are particularly noticeable in the polymerization of β-(N-piperidyl)-ethyl-methacrylate in the presence of copper stearate, as can be seen from the data presented in table 2.3 and Fig. 2.4. A composition consisting of an amino-containing monomer, structuring agent, benzoyl peroxide and copper stearate is polymerized to complete conversion without loss of monomer at 28°C in 30-40 min.

Polymerization time, sec·10^{-3}
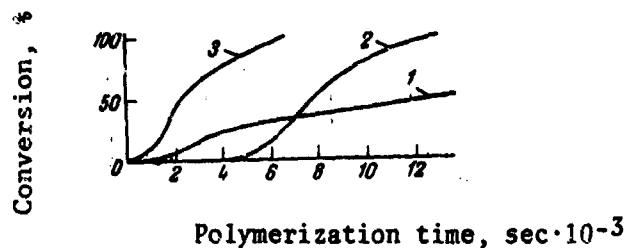
Fig. 2.4. Kinetics of Polymerization of β-(N-piperidyl)-ethyl-methacrylate at 28°C in the presence of Benzoyl Peroxide and Additives: 1. 10% black; 2. 0.5% cooper stearate; 3. 10% black and 0.5% copper stearate.

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[1] Morozova, Ye. M., Author's Abstract of Dissertation, Academy of Sciences, USSR, 1969.

The observed action of black can be explained by its structuring effect on the polymerizing system due to the forces of intermolecular inter- action. This decreases the diffusion of oxygen in the monomer layer and thus reduces the induction period, also facilitating an increase in the polymerization rate with slight conversions.

Table 2.3. Influence of addition of black on induction period of polymeriza- tion of β-(N-piperidyl)-ethyl-methacrylate at polymerization temperature 28°C in the presence of various initiators.

Black Concentration, %	Initiator	Induction Period, min
0	Benzoil Peroxide[1]	Polymerization not Observed
0	Benzoil Perioxide, Copper Stearate[2]	65
10	Benzoil Peroxide	6
10	Benzoil Peroxide, Copper Stearate	2

[1] 0.5 mol. %
[2] 0.3% as copper

The development of the structure is influenced by a change in yield point[1] of the β-(N-piperidy.,-ethyl-methacrylate with the introduction of various black additives, which can be seen from the data presented below:

black concentration, %	0.0	1.5	5.0	10.0
yield point, n/m^2	0.0	0.6	1.5	3.0

Aerosils of various types have an even greater structuring effect. For example, the yield point[1] of β-(N-piperidyl)-ethyl-acrylate changes significantly with the introduction of various quantities of "degussa M-300" aerosil, as we can see from the data presented below:

Aerosil concentration, %	0.0	1.5	3.0	5.0	7.0	10.0
Yield point, m/m^2	0.0	0.8	1.5	7.2	36.0	60.0

The viscosity of the initial system can also be increased by introducing a polymer thickener, for example, an acrylic series telomer with a molecular

[1] Yield point determined at 24°C.

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weight of 3,000 (Fig. 2.5). Fig. 2.5 shows clearly that there is an optimal concentration of thickener, at which polymerization occurs most actively; as this concentration is exceeded, polymerization is retarded. The value of the optimal concentration must be selected experimentally in each individual case.

It can be assumed that this effect, as in the case of addition of black, is explained by the change in the rate of diffusion of the oxygen of the air into the monomer layer.

Comparison of the results of the effects of various additives on the kinetics of film formation by aminoalkyl methacrylates during polymerization in air with the chemical resistance and hardness of the films produced has shown that the optimal condition for formation of coatings is initiation of polymerization of β-(N-piperidyl)-ethyl-methacrylate with benzoil peroxide in combination with copper stearate using carbon black as a thickening additive. The initial compositions have thixotropic properties, which facilitates their application to the substrate, and the coatings produced have the best properties.

Thickerner concentration, %
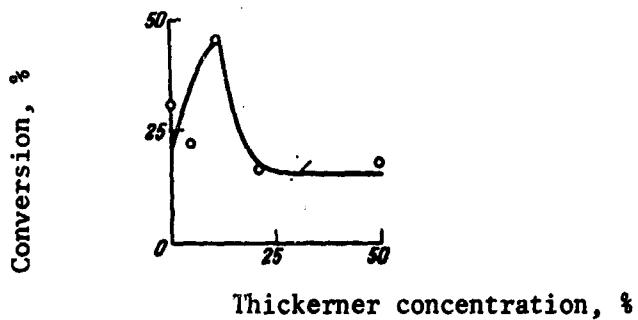
Fig. 2.5. Kinetics of Polymerization of β-(N-piperidyl)-ethyl-methacrylate in the Presence of a Thickerner at 44°C, Coating Thickness 50μ.

Summing up the above, we must note that in order to achieve a deep conversion with chemical initiation of polymerization of aminoalkyl methacrylates in a thin layer in air, two conditions must be observed: reduction of the activation energy of polymerization and reduction of the access of oxygen to the monomer layer by thickening.

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CHAPTER III

VARNISH AND WATER-SOLUBLE FILM FORMERS

Polymerization in an organic solvent produces two types of film formers: varnish and water-soluble. One pecularity of the production of the latter type is performance of the process in a solvent which is miscible with water and observation of conditions to provide for the production of a low-molecular polymer.

Production of Varnish Film Formers

In the process of production of these film formers, we must consider that in addition to the structure of the monomer, polymerization temperature and quantity of initiator, the type of solvent used and its quantity in the reaction mixture influence the polymerization process, and the influence of the oxygen of the air is less significant than for polymerization in a thin layer.

The influence of the type and quantity of solvent is manifested in that when it is introduced the concentration of monomer in the polymerizing system decreases and the rate of polymerization is reduced. The rise in viscosity in this case occurs more slowly, while the conversion of the monomer to polymer is more complete.

Solvents containing mobile hydrogen or halogen atoms, for example, carbon tetrachloride, isopropyl benzene, etc. take part in the reaction of chain transfer, which is achieved as follows:

$$R'-[-M-]_n-CH_2-\overset{\cdot}{C}H + CCl_4 \longrightarrow$$
$$\underset{R}{\big|}$$

$$\longrightarrow R'-[-M-]_n-CH_2-CH-Cl + \cdot CCl_3$$
$$\underset{R}{\big|}$$

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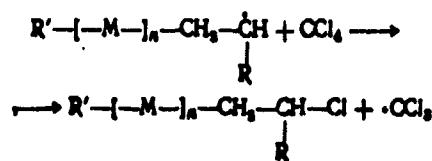
In this case, the rate of chain transfer depends on the type of solvent used; for example, the chain transfer reaction rate constants k of various solvents in the case of polymerization of methylmethacrylate at 80°C are as follows[1]:

Solvent	k, $1 \cdot mol^{-1} \cdot sec^{-1}$
Carbontetracholoride	24
Isopropyl benzene	19
Methylethylketone	7
Toluene	5.3
n-butanol	2.5
Acetone	2.25
Benzene	0.75

Solvents with high chain transfer rate constants are used in telomerization reactions to produce low-molecular polymers which are then cured by reactions of the functional groups.

The influence of the monomer structure on the rate of the chain growth and structure of the polymer must also be considered in performing polymerization in an organic solvent.

The reactivity of monomers is greatly influenced, first of all by the quantity, size and nature of the substituents present at the double bond, and also by stabilization of the monomer resulting from the effect of a conjugate double bond with a substituent. The latter dependence is quantatively expressed in the form of the thermochemical deviations from additiveness of (ΔQ) [2].

The capability of a monomer for homopolymerization is determined by the combination of reactivities of the monomer and the radical. The greater the value of ΔQ for the monomer, the less active the radical, the activity of the radical decreasing significantly more rapidly than the activity of the monomer increases. Consequently, as ΔQ increases, the rate of polymerization decreases, which can be seen from the data presented in table 3.1.

Another important factor determining the reactivity of monomers is the capability of the substituent to polarize the double bond; polarization may be caused both by electron donor and by electron acceptor groups.

Electron donor groups (alkyl, aryl, alkoxyl and other groups) increase the electron density of the double bond. Electron acceptor groups (nitryl, carbonyl, carboxyl and other groups) decrease the electron density at the double bond.

Table 3.1. Thermochemical Deviations from Additiveness and Growth Constants of Chain for Certain Monomers.

Monomer	ΔQ, kcal/mol (kg/mol)		k_p, $1 \cdot mol^{-1} \cdot sec^{-1}$
Vinylacetate	0	(0)	1700
Acrylonitryl	-	-	1340
Methylacrylate	-	-	1260
Methymethacrylate	2.4	(10.1)	513
Styrene	4.1	(17.2)	190
Methacrylonitryl	-	-	190
Butadyene	5.2	(21.8)	105
Isoprene	7.4	(31.0)	50

It has been established that substituents can be placed in the following sequence as concerns their influence on the reactivity of olefins:

$$-OR > -OCOCH_3 > -Cl > -COOR > -CN > -COCH_3 > -C_6H_5$$

The reactivity of monomers depends also on steric factors, for example when a subsitituent appears at the α-carbon atom; the rate of polymerization is significantly decreased (see table 3.1).

The influence of the initiator consists not only in initiation of the reaction of chain growth, but also in its participation in the reaction of chain transfer. This is most sharply expressed in the case of oil-soluble peroxide initiators (benzoil peroxide, tert-butyl, acetyl, lauryl, isopropil benzene hydroperoxide, etc). Oxidation-reduction initiating systems, which allow polymerization to be produced at high rates at low temperatures, are quite popular. The mechanism of action of these systems is discussed in Chapter 2.

In recent times, peroxycarbonic acid esters have become popular as polymerization initiators [3-5]:

$$RO-CO-O-O-CO-OR$$

These esters decompose into free radicals by breaking the -0-0- bond at 20-40°C. One example of such an initiator is dicyclohexyl peroxydicarbonate.

The azonitriles, frequently used as polymerization initiators in organic solvents, practically do not participate in chain transfer [6,7].

The influence of regulators of molecular weight is similar to the influence of solvents with high values of chain transfer constant. The use of regulators leads not only to a decrease in molecular weight, but also to a decrease in polydispersion and branching of the polymer. This results from the fact that the transfer of the chain through the polymer, causing the formation of branched polymers, occurs to a lesser extent than chain transfer through the regulator.

The most frequently used regulators are primary and tertiary mercaptans with at least 4 carbon atoms, as well as disulfides, diazothioesters, etc.

Formation of Coatings of Varnish Film Formers

Film formation from a polymer solution occurs in several stages [8]. In the first stage of the process, evaporation of the solvent from the free surface of the liquid occurs; the rate of evaporation of the solvent depends on its saturated vapor pressure at the evaporation temperature.

During the process of formation of coatings, the density of the solution at the evaporation surface increases, causing convective currents in the solution, equalizing the concentration of polymer through the thickness of the solution. The intensity of convective mixing gradually decreases, and at certain concentrations of the polymer the solution coagulates, beginning at the surface and extending into the depth of the solution.

In the second stage, the solvent evaporates by diffusing through the coagulated gel layer. The increasing number of contacts between structural elements of the polymer gradually causes contraction of the system; this causes the thickness of the coating to decrease.

In the last stage of film formation, the polymer coating becomes bonded to the substrate, resulting in orientation of the structural elements of the polymer and causing internal stresses in the coating, which are always directed against the forces of adhesion and in some cases may cause separation of the coating from the substrate.

The polarization optical method, developed by Shreyner and Zubov [9,10], or the cantilever method [11], based on measurement of the deflection of the free end of a cantilever-fastened elastic substrate coated with a solution of film former can be used to determine the internal stresses in paint and varnish coatings. In the cantilever method, as the solvent evaporates from the film, internal stresses arise, which force the free end of the cantilever to bend from its initial position.

The determining factor in the film formation process is the rate of evaporation of the solvent. Therefore, the following demands must be placed on solvents [12,13]: high dissolving capacity for the polymer, complete mixing with all components of the film former, low viscosity, inertness in relation to the film former, fire safety, non-toxicity and low cost.

The best version of production of paint and varnish materials is film formation from solvents in which the polymer is easily soluble and its macromolecules are branched. Evaporation is performed so that the conformation and mutual placement of the macromolecules changes to the minimum extent. This produces coatings having low vapor permeability, high adhesion and optical physical and mechanical properties.

In recent times, articles have appeared in the literature [14-16] in which the mechanism of film formation from polymer solutions is studied from the point of view of new concepts of the structure of amorphous polymers, first formulated by Kargin, Kitaygorodskiy and Slonimskiy [17].

According to these concepts, in the early stages of formation of polymer bodies -- in solutions, in melts and even in the process of polymerization -- supermolecular structures arise. Electron microscope studies of various polymers have revealed a wide variety of supermolecular structures, which Kargin [18] subdivides into globular, banded, fibrillar and spherolite structures.

The structures formed in the polymer determine the properties of the material. Slonimskiy [18], using the example of polyarylates, showed that polymers of identical chemical composition, but with diffurent supermolecular structures (globular and fibrillar), have different mechanical properties.

The production of polymers with predetermined supermolecular structure is performed by various physical methods of structure conversion [20-22], and also by synthesis under defined conditions [19].

In order to give the film formers the capability for cross linking and other specific properties, they are modified by introduction of functional groups to the macromolecules. Modification is conducted either by copolymerization of the basic components of the film former with a small quantity of modifying monomer, or grafting of this monomer to the macromolecule of film former.

By introducing the corresponding functional groups to the molecule of film-forming polymer, the coating can be given increased resistance to light or cold, increased biological activity, improved heat resistance, adhesion, dielectric properties or resistance to various corrosive media.

The study of the influence of the nature and quantity of functional groups on the properties of film formers allows us to change the properties of coatings by proper synthesis.

One of the most important properties of film formers, determining the protective properties of coatings is its adhesion [23,24]; therefore, the greatest number of investigations has been designed to determine the dependences between adhesion and the content of functional groups in a polymer [25-29]. McLaren and Seiler [26] discovered that the adhesion of vinyl polymers to cellophane is proportional to the concentration of carboxyl groups in the polymer.

The increase in adhesion strength with increasing carboxyl group concentration is also observed in studies of the adhesion of copolymers of ethylene with acrylic acid to copper, aluminum and steel [30].

The introduction of functional groups with non-paired electrons to the composition of a polymer significantly increases the adhesion of the polymer. This was shown by Mao and Reegen [31], who determine the layer separation resistance of copolymers of methylmethacrylate with secondary and tertiary aminoalkyl methacrylates (Table 3.2).

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Table 3.2. Layer separation resistance of copolymers of methylmethacrylate with aminoalkyl methacrylate.

Monomer	Concentration, Mol. %	Layer Separation Resistance, gs/cm
Dimethylaminomethacrylate	10	Does not Separate
	5	375
tert-butylaminoathylmethacrylate	10	Does not Separate
	5	350
	2	320

Note. Separation resistance of polybutyl methacrylate 160 g/cm.

A study [31] of the influence of the size of the alkyl radical on adhesion of a coating based on copolymers of methylmethacrylate with alkyl acrylates and alkylmethacrylates to an epoxy primer (3.1) showed that in the case of copolymers with alkylacrylates, the separation strength increases monotonically up to octylacrylate, after which a tendency is observed toward retention of a constant value of separation force. In the case of copolymers with alkylmethacrylates, the separation force increases with increasing number of carbon atoms in the side chain of the alkylmethacrylate. A similar tendency has also been observed by other researchers [32,33].
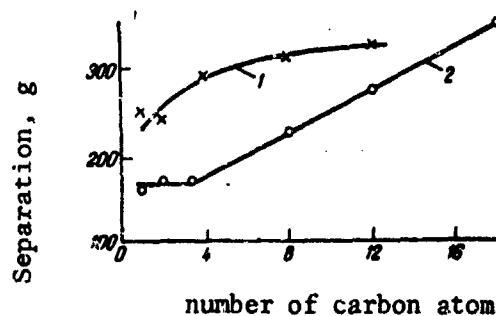
Fig. 3.1. Separation Force of Coatings as a Function of Alkyl Radical in Copolymers of Methylmethacrylate with: 1, Alkylacrylate; 2, Alkylmethacrylate.

A study of the separation of coatings based on copolymers of methylmethacrylate containing carboxyl and amide groups showed (Fig. 3.2) that for copolymers with acrylic acid, the separation resistance increases with increasing molar concentration of the acid in the copolymer. The introduction of acrylamide to the copolymer increases the adhesion with a content of up to 10 mol. % acrylamide. Further increases in the concentration of acrylamide in the copolymer cause a reduction of adhesion, which the authors explain by the increased degree of crystallinity of the polymer. The introduction of methacrylic acid and methacrylamide to the copolymer increases the adhesion slightly; when their content is over 5 mol.%, adhesion decreases sharply.
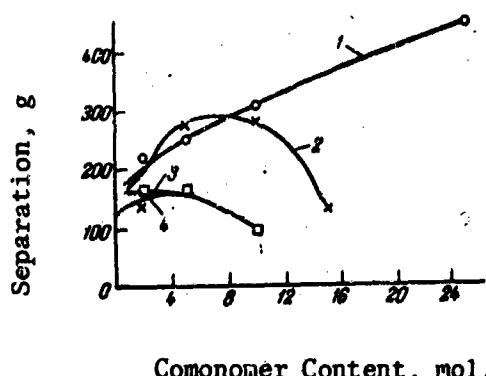
Fig. 3.2. Separation Force of Coating Based on Methylmethacrylate
as a function of Type and Content of Comonomer: 1. Acrylic Acid;
2. Acrylomide; 3. Methacrylic Acid; 4. Methacrylomide.

The dependence of adhesion strength on functional group content dis-
covered by a number of authors can be explained by a decrease in the mobility
of segments of polymer macromolecules with increasing content of polar groups,
which decreases the probability of contact of functional adhesive groups
and the substrate, and also causes internal stresses to arise in the coating,
acting against the forces of adhesion. If a rigid polymer is taken as the
base, when a component is introduced to its composition which gives the
polymer elasticity, a monotonic increase in adhesion strength with increasing
concentration of this component can be achieved.

The literature contains data on the influence of various functional
groups on other properties of film formers as well; however, these data are
only qualitative, since the studies were performed with various types of
polymers of various molecular weights with various contents of functional
groups]37], [38].

A quantative study [39] of the influence of the type of functional group
on the properties of film formers showed that the introduction of like
quantities (3-5%) of methacrylic monomers containing carboxylic, amide,
hydroxyl, glycidyl, methylene, amine, nitrile and other functional groups
to polybutyl methacrylate macromolecules as a significantly different influence
on the mechanical and protective properties, adhesion, moisture absorption
and vapor permeability of the coatings.

-88-
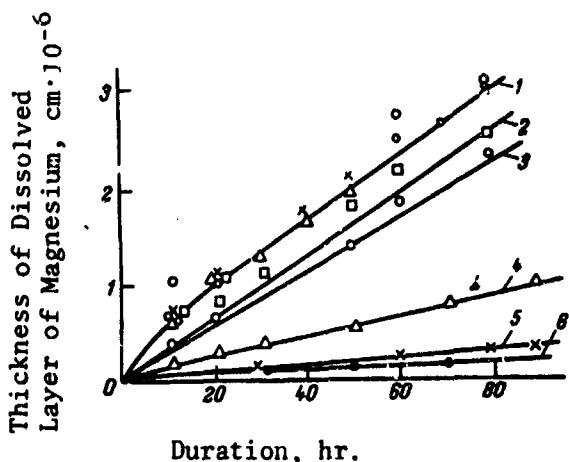
Fig. 3.3. Rate of Corrosion of Magnesium Alloys as a Function of Duration of Exposure to Air with 98% Relative Humidity Beneath Coatings Based on Copolymers of Polybutyl Methacrylate: 1. With Dymethyl Aminoethyl Methacrylate; 2. With Methalene Methacrylamide; 3. With Acryclonitrile; 4. With Methacrylamide; 5. Without Comonomer; 6. With Glycidyl methacrylate.

The introduction of methylene, glycide, hydroxyl amine and carboxyl groups increases the adhesion to the metal. The introduction of amide groups has practically no influence on adhesion; nitrile groups decrease adhesion, although only slightly. This influence of functional groups on adhesion is related both to their specific interaction with the substrate material, and to the internal stresses arising in formation of the coatings.

The moisture absorption of coatings depends directly on the hydrofelicity of the functional monomers. The maximum moisture absorption is that of copolymers containing tertiary amino groups.

In a pure, moist atmosphere, the protective properties are determined by the adhesion and moisture absorption of the coating. The best protective properties (Fig. 3.3) are shown by a copolymer with glycidyl methacrylate which is explained, apparently, by its hydrophobicity, assuring retention of the adhesion bond of the coating to the substrate in a moist atmosphere. The low protective properties of copolymers with dimethyl aminoethyl methacrylate and methalene methacrylimide can be explained by the presence of 4-valent positive nitrogen in the side chain of these monomers, causing an increase in water absorption of the coating, leading to weakening of its adhesion in a moist atmosphere.

-89-
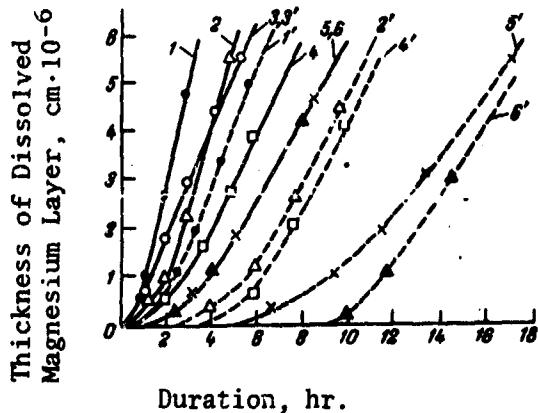
Fig. 3.4. Rate of Corrosion of Magnesium Alloys as a Function of Duration of Application of Vapors from 26% Solution of Hydrochloric Acid on Coating and Free films of Copolymer of Polybutyl methacrylate: 1, 1', Without Comonomer; 2,2', With Methacrylamide; 3,3', With Acrylonitrile; 4,4', With Methacrylamide; 5, 5', With Glycidyl Methacrylate; 6, 6'. With Dimethyl Aminoethyl methacrylate.

In an atmosphere of hydrochloric acid vapors, the influence of functional groups on the protective properties of coatings results basically from chemical interaction of these groups with the hydrochloric acid (Fig. 3.4), and the significance of adhesion and of moisture absorption decreases significantly.

The best protective properties are those of copolymers with dimethyl aminoethyl methacrylate and glycidyl methacrylate, after which the protective properties decrease from methalene methacrylamide to butylmethacrylate; the same is observed for free films based on these copolymers.

Production of Water-Soluble Film Formers

Recently, the problem of the production of water-soluble film formers [40-47] and their properties has been given considerable attention. Most of the methods of synthesis of water-soluble polymers described call for controlled polymerization in a water-miscible organic solvent with subsequent dilution of the products produced with water.

In connection with this, when water-soluble film formers, are produced, all of the regularities of varnish polymerization described above remain in force.

Water-soluble film formers are produced by copolymerization of vinyl monomers with monomers containing hydrophillic functional groups, which improve the solubility of the copolymer produced in water. Therefore, the basic types of such film formers can be divided as follows: acid-soluble, nonionic and alkali-soluble.

-90-

Acid-soluble film formers are produced by copolymerization with monomers for which the dissolving agent is an acid (acetic or hydrochloric). The most suitable of this class of monomers are acrylamide and aminoalkyl acrylates [43, 49, 50, 51]. In principle, acid-soluble film formers can be used in the application of coatings by the method of electrodeposition, but at the present time, they have not become widely used due to the corrosion which arises when they are applied to a metal substrate.

Nonionic film formers are produced by copolymerization of alkylacrylates with hydroxalkyl-containing monomers; therefore, coatings based on them have high sensitivity to moisture. They can be produced by using oxyalkyl acrylates and oxyalkyl methacrylates copolymerized with lower alkylacrylates, as well as copolymers of styrene with allyl alcohol [52] and copolymers of hydroxalkyl methacrylates with monoethylene glycol methacrylate [53].

Alkali-soluble film formers are produced by copolymerization of vinylic and acrylic monomers with monomers containing carboxyl groups. The monomers most frequently used are acrylic and methacrylic acid, as well as maleic anhydride and its derivatives. This type of film former is dissolved in aqueous alkali solutions; the solutions have their optimal properties with 90-100% neutralization of all carboxyl groups [54].

Of the various types of water-soluble film formers, only the alkali-soluble types have become widely used and have been studied in detail. Thermo-reactive alkali-soluble film formers are known, the use of which requires that curing agents be used. Self-cross-linking types are also known, containing two types of functional groups. Both types will be specially studied in Chapter 6.
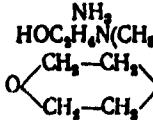
When alkali-soluble film formers are used, considerable attention must be given to such problems as: the selection of a neutralizing base, the role of the organic solvent, the molecular weight of the polymer, and the number of carboxyl groups introduced.

The nature of the neutralizing base influences the viscosity of the solution produced, its stability upon storage, and also the properties of the coatings -- the curing rate, degree of swelling and durability.

The neutralizing base must interact with the water-soluble polymer produced and must have low volatility [55]. The properties of bases most frequently used to produce alkali-soluble film formers are presented in Table 3.3.

In many cases, inorganic bases are used, frequently together with tri-ethylamine [40].

Table 3.3. Properties of Bases Used for Production of Alkali-Soluble Film Formers

Overall Base		Mol. wt.	B. P. °C	Density, d_4^{20}	Vapor Pressure at 20°C mm Hg
Name	Right Formula				
Ammonia	NH_3	17,03	—	--	—
Dimethylethanolamine	$HOC_2H_4N(CH_3)_2$	39,14	134,1	0,8879	4,4
Morpholine	$O{\diagup}{CH_2-CH_2 \atop CH_2-CH_2}{\diagdown}NH$	37,12	128,2	1,0020	7,0
Triethanolamine	$N(CH_2CH_2OH)_3$	149,19	335,4	1,1258	0,1
Triethylamine	$N(C_2H_5)_3$	101,19	89,5	0,7290	—
Ethanolamine	$HOCH_2CH_2NH_2$	61,08	170,4	1,0179	1

The nature of the monomers used influences the ability of the products produced to dissolve in water. For example, the minimum quantity of carboxyl groups necessary for the production of alkali-soluble acrylate film formers depends on the hydrophobicity of the basic monomer [56]: the quantity of methacrylic acid increases in order from methylacrylate, ethylacrylate to butylacrylate.

In addition to other factors, the ability of the polymer to dissolve in aqueous alkali solutions is significantly influenced by the molecular weight. With high molecular weight of the polymer, its solubility can be increased by introducing a large number of carboxyl groups to the molecule which, however, worsens the film-forming properties of the polymer. Thus, for each film former, a molecular weight must be found which provides solubility in aqueous alkali solutions upon introduction of the necessary quantity of carboxyl groups to the polymer molecule. It has been shown [57] that the molecular weight of water-soluble carboxyl-containing polyacrylates fluctuates between 6,000 and 30,000. Decreased molecular weight is achieved by using regulators in the polymerization process, for example thioglycolic acid, or more frequently isopropil alcohol [57], which, mixing with the water, at the same time acts as a solvent and chain transfer agent. Alkylmercaptans [58] such as butyl-octyl-and dodecylmorcaptans are frequently used as chain transfer agents.

The presence of the organic solvent in the system decreases the viscosity and increases the stability of the alkaline solution of film former. The most suitable solvents are alcohols, simple and complex esters, ketones [40], as well as dimethylformamide and dimethylsulfoxide [59].

The copolymers of the lower esters of acrylic acid with methacrylic acid can be produced with no organic solvent [60-61] by the method of non-emulsifier polymerization (see Chapter 1).

Formation of Coatings of Water-Soluble Film Formers

The process of formation of coatings from water-soluble film formers has a number of pecularities resulting from the replacement of the organic solvent with water. The drying time of water soluble paint and varnish materials is longer [62] than that of varnish materials, since the evaporation of water requires a greater quantity of heat (about 620 cal/g) than the evaporation of organic solvents (120-150 cal/g). Evaporation of water is slowed by high relative humidity. Furthermore, water has a high value of surface tension (72 erg/cm^2), preventing good spreading of the paint when applied by ordinary methods.

The high dielectric constant of water, as well as the capability of water-soluble film formers of dissolving into ions (R-COO$^-$, H$^+$ or NH$_4^+$) under the influence of electric current allows them to be applied to the surface being painted by electrodeposition [63-70], which is currently broadly used in various branches of industry, particularly the motor vehicle industry. This method has a number of advantages over other known methods of application of film formers (spraying, dipping, etc.), including: full automation of the painting process, reduction of the consumption of film formers, improvement of sanitary working conditions, reduction of the fire danger in painting shops, low water content in the coating and possibility of testing coating thickness [71].

The essence of the method is that the product to be painted is submerged in a bath containing the water-soluble film-forming material and a direct electric current is passed through. The body of the bath serves as the anode, the product being painted as the cathode. Each polymer molecule, which is negatively charged (R-COO$^-$), moves through the field of the electric current to the anode and is deposited on it in the form of a water-insoluble acid (R-COOH) or, if it interacts with the metal of the anode, as an insoluble salt (R-COOMe).

When coatings are formed by electrodeposition, several processes occur simultaneously: electrolysis, electrophoresis and electrosmosis. In the case of electrodeposition of film formers consisting of aqueous solutions, the process of electrolysis predominates.

The properties of the coatings formed depend on a number of factors [72-76].

The pH of the medium influences the thickness of the coating produced. For example, for carboxyl-containing acrylate film formers, the thickness of coatings is sharply decreased as the pH of the medium is increased [77]. Furthermore, at high values of pH (pH>11), electrolysis of water begins, causing liberation of gas at the anode, which prevents the formation of a continuous coating. At low values of pH, many alkali-soluble polymers lose the ability to dissolve [70]. This makes it necessary to select optimal pH values to provide the maximum stability of the system and thickness of the coating.

In addition to the pH value, the quality of the film is also influenced by such parameters as: applied voltage, temperature and concentration of bath, presence of organic solvent [78]. The voltage applied is directly related to the quantity of material precipitated. The low conductivity of aqueous solutions of film formers used allow coatings to be deposited at high voltages. It has been established that the higher the voltage used in electro-deposition, the better the dissipating ability[1] of the working solution and, consequently, the greater the thickness of the film and the better its corrosion resistance. High dissipating ability allows products of complex configurations to be painted [79].

As the bath temperature is increased, the mobility of the ions increases (since viscosity decreases), and the quantity of material deposited increases [78]. The concentration of the bath influences the quantity of material deposited differently for different polymers. High polymer concentrations in the bath are not recommended, since this results in increased viscosity and consequently in decreased ion mobility. It has been demonstrated that the optimal concentration is that which provides the maximum conductivity of the system and minimum viscosity.

The presence of an organic solvent in small quantities frequently has a positive influence, decreasing the viscosity of the solutions studied. Furthermore, the presence of an organic solvent improves the shine on the coatings produced. The selection of an additional organic solvent depends on the type of film former used. It has been discovered [81] that the most effective solvents are polar solvents such as alcohols or cellosolves.

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[1] The ability of a polymer solution to form a coating of even thickness.

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CHAPTER IV

AGING OF POLYMER FILM FORMERS AND THEIR RESISTANCE TO VARIOUS INFLUENCES

As they are used, polymer coatings are subjected to chemical and mechanical influences, as well as the effects of heat, light, microorganisms and various types of radiation. All of these processes lead to aging of the coatings. As this occurs, such qualities of the coating as elasticity, strength and external appearance change. The resistance of the coatings to the influence of these factors depends on the structure and chemical composition of the film former. For example, carbon-chain polymers, the basic chains of the macromolecules of which are constructed of carbon atoms, are highly resistant to the effects of acids, alkalis and salts. At the same time, heterochain polymers, the main chains of the macromolecules of which contain carbon atoms plus oxygen, nitrogen, etc., are easily broken down under the influence of these chemical reagents. Polymers in the crystalline state react with chemical agents more slowly than in the amorphous state.

Processes related to the aging of high molecular compounds of various classes have been studied in detail, and the results of these studies have been presented in a number of special monographs and reviews [1-13].

In this chapter, we will study the aging of polymerization coatings, the production of which has been described in the preceding chapters.

Thermal, Thermal-Oxidative and Photochemical Destruction of Coatings

During the process of exposure of coatings to atmospheric conditions, they are subjected simultaneously to the influence of high temperatures, the oxygen in the air and ultraviolet radiation. This results in both physical and chemical conversion of the high molecular compounds. Elevated temperatures change primarily the physical state of the polymer (movement of macromolecules and their segments); when exposed to the oxygen of the air and ultraviolet radiation, chemical conversion of the polymers occurs.

The nature and rate of the chemical conversions are basically related to the structure of the macromolecule. Thus, in some vinylic polymers containing reactive groups (polyvinylic alcohol, polyvinyl chloride, polyvinyl acetate), the bonds with the side substituents are changed, while the main chain remains constant. Thermal destruction of polystyrene, polymethylmethacrylate, polyisobutylene and polybutyldiene cause breaks in the main chain of the macromolecules, and the end product of the destruction is the initial monomers or compounds similar to them in composition [1].

Based on modern conceptions, the process of thermal destruction of carbon chain polymers can be looked upon as a series of successive elementary reactions occurring by the free radical chain mechanism.

Paint and varnish coatings are most frequently used under atmospheric conditions; therefore, thermal destruction is accompanied by oxidative processes. As we know, the destruction of high molecular compounds when they are heated in the presence of oxygen in many cases occurs significantly more rapidly than in an inert atmosphere, and begins at lower temperatures. For example, the destruction of polymethylmethacrylate in the presence of oxygen beings at a temperature of 200°C, whereas in an inert atmosphere it begins at 250°C. The reduction in molecular weight without liberation of monomers observed in this case indicates that the destruction occurs due to break down of chains at the point of formation of peroxides [14].

A clear illustration of the fact that molecular weight and polymer structure are changed during thermal-oxidative destruction can be found in the results of aging of certain acrylic and vinylic polymers at 150°C. For example, coatings of polybutyl acrylate following heating become insoluble in ethylacetate, indicating the development of a reticular structure. Coatings based on polyethyl acrylate continue to be soluble in ethyl acetate, but form more viscous solutions than before heating; coatings based on polyvinyl acetate are also soluble, but form solutions of lower viscosity than before heating, indicating destruction of the main macromolecular chain of the polymer. Polyvinyl acetate coatings have the greatest resistance to thermal-oxidative destruction; the properties of these coatings remain practically unchanged after heating.

It is known that the life of carbon chain polymers depends to a great extent on their chemical structure. Polymers containing the tertiary carbon atom are more easily oxidized than polymers containing the secondary and primary carbon atoms.

The presence of unsaturated sectors in the polymer chains decreases the resistance of coatings to thermal oxidative destruction. In the first stages of oxidation, the oxygen is attached at the location of the double bonds and the polymer chains break apart, forming oxygen-containing macro radicals, which interaction to produce polymers with a three dimensional structure. This forms tertiary carbon atoms which facilitate further oxidation of the polymer and, subsequently, further thermal oxidative destruction.

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When coatings are exposed to atmospheric conditions, the oxygen of the air acts together with sunlight, heat and moisture. One of the main reasons for deterioration in the properties of polymers under these conditions is photochemical destruction.

In contrast to thermal destruction, during photochemical destruction, the molecules absorb energy quanta with frequency ν. If the energy of the light is high enough, the chemical bonds are broken and further development of the chain process is facilitated.

The degree of photochemical destruction depends on the chemical composition of the polymer, wave length and intensity of the radiation. For example, the properties of coatings based on polystyrene following extended exposure to diffuse light even at 100°C do not change, whereas at 60°C, ultraviolet light causes yellowing of the coating (in the presence of oxygen) [4]

Polystyrene and polymethacrylates are polymers distinguished by relatively high resistance to photo-oxidative destruction. For example, following 5 years exposure of coatings based on polymeth, harrylate under various climatic conditions from the tropics to the arctic, no reduction in protective properties was observed [10].

The resistance of polymers to thermal, thermal oxidative and photo oxidative destruction can be increased by introducing antioxidants such as phenols or amines to the polymer [1-5]. The mechanism of the action of various types of antioxidants and their effectiveness have been studied in detail in the literature [1-5].

Resistance to the Effects of Chemical Reagents

The resistance of polymers to various chemical reagents depends primarily on the chemical composition, to a lesser extent on the structure of the polymers [1,9,10,15-21]. For example, carbon chain polymers and copolymers are resistant to the effects of acids, bases, water, salts and polar solvents, but dissolve in nonpolar solvents. Replacement of the hydrogen atom in the -OH, -COOH, -NH2, and -CONH2 groups results in rapid aging of polymers when exposed to water, acids, bases and polar solvents, but increases their resistance to the effects of nonpolar solvents. For example, polymers and copolymers based on α, β-unsaturated acids (acrylic, methacrylic) swell and dissolve in water, polar organic solvents, acids and bases, but are resistant to nonpolar solvents.

When the hydrogen atom in the polyethylene chain is replaced by atoms of Cl or F, the resistance to the effects of alkalis, acids and water is retained; in the case of fluorine derivatives, the resistance is higher than that of the carbon chain polymers. For example, polytetrafluoroethylene does not change its properties with extended exposure to water, organic solvents, strong oxidants, or even heated, concentrated solution of acids and alkalis. When fuming sulfuric and nitric acids act on polyethylene at room temperature, its mechanical properties are changed, and at high temperatures, carbonization

occurs [10]. Polyethylene swells in aliphatic aromatic and various chlorinated hydrocarbons, causing a change in its mechanical properties.

Carbon chain polymers with a double bond in the macromolecular chain (natural rubber, polychloroprene) are less resistant to the effects of chemical reagents, and particularly to the effects of oxidants.

During alkaline hydrolysis of homopolymers and copolymers of methacrylamide with methacrylic acid, it was discovered that in this case only 70% of the amide groups are hydrolysed. The authors explain this variously. Arcus [18] believes that the moderation of hydrolysis of the copolymer of methacrylamide and methacrylic acid results from the formation of hydrogen bonds between the carboxyl and residual amide groups, and that full interruption of hydrolysis should occur when each remaining amide group is blocked on both sides with carboxyl groups:

$$\cdots-CH_2-\underset{\underset{\underset{-O\cdots H-N-H\cdots O^-}{C=O}}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{C=O}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\underset{\underset{C=O}{|}}{\overset{\overset{CH_3}{|}}{C}}-\cdots$$
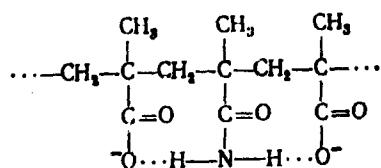
The resistance of various polymers to certain media is presented in Table 4.1.

Table 4.1. Resistance of Certain Polymers in Various Media [10].

Polymer	Water	Alkali	Acid	Oxident	Organic Solvent
Polyethylene	1	1	1	1	3
Polyisobutylene	1	1	1	1	3
Polystyrene	1	1	1	3	3
Polyvinylchloride	1	1	1	1	2
Copolymer of vinyl acetate and vinyl Chloride	1	1	1	2	2
Polyvinyl acetate	2	3	3	3	3
Polyvinyl alcohol	3	3	3	3	2
Polyacrylic acid	3	3	3	3	2
Polymethyl acrylate	1	3	2	3	2
Polymethyl methacrylate	1	1	1	3	2
Butyl rubber	1	1	1	2	3
Copolymer of butadyene with styrene	1	1	1	3	3
Copolymer of butadyene with acrylonitrile	1	1	1	3	2

Symbols: 1. Stable; 2. Somewhat Stable; 3. Unstable.

Aging Under the Influence of Ionizing Radiation

The influence of various types of ionizing radiation (x-rays, gamma-rays, electrons, α-radiation, etc.), like other influences (heat, light, chemical reagents) causes chemical reactions to occur in polymers, leading to processes of aging. In recent years, broad scale studies of aging of high polymer compounds of various classes under the influence of radiation have been conducted [6,7,22-24].

Ionizing radiation forms ions and excited molecules, the dissociation of which produces two free radicals or two molecular fragments. These free radicals may enter into various reactions: recombination, disproportionation separation of a hydrogen atom, attachment of oxygen. These reactions cause either destruction or cross-linking of the polymer, changing its physical and chemical structure.

The resistance of polymers to the influence of ionizing radiation is determined by their chemical structure. The greatest radiation stability is shown by polymers containing aromatic rings, the least -- by polymers constructed of olephatic links. The polymers can be placed in the following sequence of decreasing radiation resistance: polystyrene, polyethylene, polyamides, polyvinyl chloride, polymethylmethacrylate, polytetrafluoroethylene [23]. It has also been noted that the organic polymers containing the quarternary carbon atom in the basic macromolecular chain (polymethylmethacrylate, polyisobutylene) or containing a halide atom has a subsituient at the carbon atom next to the methylene group (polyvinylidene chloride, polytetrafluoroethylene, polyvinyl fluoride, etc.) are primarily damaged. Polymers containing at least one hydrogen atom at the carbon atom next to the methylene group (polystyrene, polyvinyl acetate, polyethylene, polycaprolactan, polyacrylates, etc.) are primarily cross linked by radiation.

The behavior of polymers during irradiation is also influenced by the nature and structure of the side carbon chain. For example, [25,26], polymethylmethacrylate is destroyed under the influence of radiation, while polyalkylmethacrylates with 12-18 carbon atoms in the side chain are cross linked. The structure of the side chain also influences the process of curing of polyacrylates. Thus, the absorbed energy, going into formation of one transverse bond for poly-n-butyl-and polyiospropyl acrylate is 190±30 ev, while for poly-n-butyl acrylate it is 600 ev.

The placement of the double bonds in the polymer chains influences the degree of cross linking. If the double bonds are located near the end of the macromolecules, the number of cross links is considerably greater than when the double bonds are located far from the ends of the chain [27, 28].

Contradictory data have been published concerning the changes in polymer structures during irradiation. For example, Lauton [29] believes that most cross links in polyethylene are formed in amorphous areas during irradiation. However, later data indicates that cross linking occurs equally both in crystalline and in amorphous areas [30-32].

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The rate of cross linking of polyethylene and the rate of destruction of polymethylmethacrylate upon irradiation depend strongly on temperature [33-35], the rate of destruction increasing with increasing temperature.

The influence of oxygen during irradiation of polymers depends both on the nature of the polymer irradiated, and on the conditions under which irradiation occurs. Polyisobutylene, for example, undergoes destruction at the same rate both in air and in a vacuum [36]. Measurement of the content of the sol and gel fractions in polyethylene film irradiated in air has shown that the rate of destruction increases under the influence of oxygen, while the rate of cross linking remains practically unchanged [38]. The access of oxygen to the irradiated specimen is significant. For example, the quantity of oxygen dissolved in the mass of a block of polymethylmethacrylate 1 cm thick is insufficient to have a significant influence on the rate of destruction [37]. The influence of oxygen on cross-linking has been found weaker when thicker specimens are used [38, 39].

It was discovered for a number of polymers which cross link upon irradiation that cross-linking in air occurs significantly more slowly than in a vacuum.

The additives introduced to a polymer may change the behavior of the material during irradiation with high energy particles significantly. Additives and low molecular compounds can be divided according to the degree of their influence into active and inactive groups. The active additives, in turn, can be divided into materials absorbing the energy of radiation and materials which enter into chemical reactions with reactive products formed during irradiation. Dissolution of oxiquinoline, naphthaline and other aromatic compounds in the polymer decreases the destruction of polymethylmethacrylate [38]. The protective action of aromatic compounds consists in that they absorb a certain quantity of the energy of ionization or excitation and thereby decrease the degree of destruction of the polymer [38]. Sulfur and thiuram, both free and bound, moderate the process of structuring of polymers having double bonds, while black participates in the formation of the three dimensional grid under the influence of radiation [40]. The stability of paint and varnish coatings to the effects of ionizing radiation is influenced by the substrate material, as well as the nature of the pigment and plasticizer.

When 23 specimens of commercial coatings produced on various surfaces were irradiated, it was shown that coatings of polyvinylic resin on aluminum panels were damaged after irradiation at doses of up to $2 \cdot 10^8$ rad, while on concrete panels they were not damaged following doses of up to 10^9 rad, i. e., 5 times greater [41].

Data are available indicating that irradiation at doses of up to $8 \cdot 10^8$ rad has a different influence on different pigments introduced into the same resin [41]. However, when paint and varnish coatings based on polyvinyl chloride and chlorinated rubber with various pigments (white lead, titanium dioxide, antimonic oxide, berium sulfate, chromium oxide, ferric oxide, black, etc.) were tested, it was found that the behavior of all specimens was determined primarily by the stability of the binder [41]. At high

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radiation doses and at high temperatures, the pigments have a catalytic effect.

Aging under the Influence of Microorganisms

It was earlier considered that microorganisms could break down only natural high molecular compounds such as cellulose and protein, while synthetic polymers were not subject to their action. However, it was later learned that many paints and varnish materials and coatings, plastics and synthetic resins are subject to attack by microorganisms, insects and rodents. The external appearance of a mechanical, electrical and other valuable properties of the polymer materials are worsened. For example, the viscosity of latex paint and varnish materials changes significantly following the introduction of various microorganisms, as we can see from the data [42] of Table 4.2.

Table 4.2. Viscosity of Certain Latexes Before and After Introduction of Microorganisms [42].

Microorganisms	Viscosity (in Cp) of Latex Based on		
	Vinyl acetate	Styrene-butadiene	Acrylate
Before Implantation	800	750	9.5
Proteus species	250	325	4.6
Aerobacter species	220	310	5.4
Flavobacterium species	280	355	6.0

Vinylchloride polymers plasticized with dibutyl sebacinate, become brittle considerably more rapidly following exposure to mold than films not exposed to mold [43].

The resistance of polymer products to the effects of microorganisms depends primarily on the chemical composition of the polymer, but also on the nature of the plasticizer, fillers, stabilizer and other additives. Furthermore, the stability of polymers is influenced by the surrounding medium (humidity, temperature, etc.).

The influence of the chemical composition of the polymer on the resistance of coatings to microorganisms can be clearly demonstrated by the data [44-46] presented below:

Polymer	Resistance to Micro-organisms
Cellulose nitrate	weak
Ethylcellulose	good
Phenol-formaldahyde resin	"
Resorcino-formaldahyde resin	"
Phenol-analyne-formaldahyde resin	weak
Melamene-formaldahyde resin	good
Urea-formaldahyde resin	"

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Polymer	Resistance to Microorganisms
Caseine-formaldahyde resin	Weak
Polyamide (nylon 6) resin	good
Ethyleneglycolterephthalate (terylene,lavsan)	"
Gliphthalic resin	"
Epoxy resin	"
Polyethylene	"
Polymonochlorotetrafluoroethylene	"
Polyisobutylene	"
Polystyrene	"
Polyvinyl acetate	weak
Copolymer of vinyl fluoride with vinyl acetate	good
Polyvinylbutyral	"
Polyvinyladidene chloride	"
Polyvinylic alcohol	weak
Polychloroprene	good
Polymethylacrylate	"
Polyacrylonitrile	"
Copolymer of acrylonitrile with vinylchloride	"
Polymethylmethacrylate	"
Polyvinyl carbasol	"

As we can see from these data, most polymers are resistant to the effects of microorganisms.

Some authors [47] believe that technical polymers mold primarily due to the presence of various impurities and additives.

The most detailed studies have been those of the resistance of various plasticizers to the influence of microorganisms. Least resistant are derivatives of the higher fatty acids -- buteric, lauric, ricinoleic and steric. The esters and salts of mellaic and thallic acids, and also of phosphoric acid, are not subject to the influence of microorganisms [48,49]. Polyhydric alcohols are easily absorbed by mold, if hydroxyl groups are present at neighboring or nearby carbon atoms. For example, 2, 3- and 1, 4- butanediole mold more strongly than 1, 3- butanediole.

The resistance of polymer materials to the effects of microorganisms is reduced by materials added to the composition of the polymer during synthesis. (emulsifiers, catalysts, etc.).

Most inorganic additives, in particular pigments, prevent the growth of mold on polymer materials. The most effective are titanium dioxide, zinc oxide, the least effective are calcium carbonate and chromium green [49], [50]. However, pigment only partially protects the polymer film from the influence of the microorganisms; more radical protection requires that fungicides be used. However, some highly active fungicide compounds are not used. The following requirements are placed on fungicide materials: high effectiveness;

good compatibility with polymer materials; no interaction with the polymer; no facilitation of other types of aging; resistance to the effects of water; low volatility and harmlessness for man. Unfortunately, there are no fungicide compounds which completely satisfy this list of requirements. Therefore, fungicide compounds must be carefully selected for each specific case.

The most widely used fungicides are the organometallic compounds containing mercury, tin, lead, copper, bismuth, etc. Most frequently used are organic compounds of mercury, introduced primarily to paint and varnish materials designed for external use, since these compounds are toxic (their toxicity in paint and varnish products is significantly reduced due to their low volatility and solubility in water). Furthermore, they cause corrosion of aluminum and its alloys.

Among the organic copper compounds, the 8-oxiquinolinate is most frequently used. It is nontoxic, heat resistant and insoluble in water. Furthermore, it is chemically inert and does not interact with the components of the paint. Following development of a water-soluble form of the 8-oxiquinolinate, the use of this compound was significantly expanded. Copper naphthenate is insufficiently active for paint and varnish materials, but is a good fungicide for textile materials.

In addition to the organometallic compounds of copper and mercury listed above, triphenylphosphorous, triphenylantimony, triphenylbismuth, triphenyl-arsenic, zinc diethyldithiocarbamate and other quarternary ammonium salts are used [45]. Recently, considerable attention has been given to organic tin compounds, which have fungicidal and batericidal activity. Tin bis-(tri-butyl)-oxide is particularly broadly used. A number of film-forming materials resistant to microorganisms, particularly acrylates, have been synethsized using organic compounds of tin and lead [51, 52].

Among the organic compounds containing no metal atoms, the best fungicides for paint and varnish coatings are salicylanilide, pentacholorophenylate, pentacholorphenyl, n-toluene sulfonimide, hydrazine sulfate, ammonium thiocyanate, etc. [45]. However, most organic fungicides are toxic and effective only in high concentrations (10% or more).

Among the inorganic fungicides, the most frequently used are uranyl nitrate, mercuric chloride, silicon fluoride; the first two compounds are the most active.

In order to protect paint and varnish materials based on vinylchloride resin, up to 0.2% 0-phenylmercury benzine sulfimide, 0.2% phenylmercury stearate or 0.5% phenylmercury salicylate may be introduced; for materials based on methacrylic resins, 0.1% phenylmercury salicylate, 1.0% phenylmercury acetate, 1.0% phenylmercury 0-benzene sulfumide, or 1.0% pyridyl mercury stearate may be used; for latex materials, various compounds of mercury, chloroacetamide and organic tin compounds are used.

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SECTION II

MONOMERS, PAINT AND VARNISH MATERIALS AND COATINGS BASED ON THEM

Chapter V

Monomers

The monomers used for the production of polymerization film formers
can be arbitrarily divided into basic and modifying monomers. The basic
monomers determine the structure of the polymer chain and the main properties
of the film former. The modifying monomers are introduced to the composition
of copolymers to give the film formers specific properties and the ability to
form 3-dimensional structures. Modification may be performed either by co-
polymerization of the basic components of the film former with small quantities
of modifying monomer, or by grafting of this monomer to the macromolecule of
the film former.

By introducing the corresponding functional groups to the molecule of
a film-forming polymer: amine, amide, hydroxyl, epoxy, alkoxile and other
groups, the coating can be given increased light or cold resistance, biologi-
cal activity, heat resistance, adhesion, dielectric properties or resistance
to the affects of various corrosive media. Film formers with many valuable
properties are produced by copolymerization of basic monomers with certain
elementary organic monomers.

We present below the characteristics and methods of production of monomers
most frequently used in the synthesis of polymerization film formers. The
properties and methods of production of those synthesized recently, which are
of the greatest interest, are presented in detail.

Basic Monomers

Acrylic and methacrylic acid alkyl esters (alkyl acrylates and alkyl
methacrylates) are promising for the synthesis of polymerization film formers,
since they are used to produce elastic coatings with high resistance to at-
mospheric influences. The introduction of lower methacrylates to the composi-
tion of the polymer, furthermore, increases the hardness of the coating and
its resistance to the effects of chemical reagents.

Alkyl acrylates and alkyl methacrylates are colorless, transparent liquids with a characteristic odor, stronger in the acrylates.

At the present time, alkyl acrylates are produced industrially by the following methods:

1. From acetylene, carbon monoxide and alcohol by the Reppe [transliteration -- correct spelling unknown] method:

$$4HC{\equiv}CH + 4ROH + Ni(CO)_4 + 2HCl \longrightarrow$$
$$\longrightarrow 4CH_2{=}CHCOOR + H_2 + NiCl_2$$
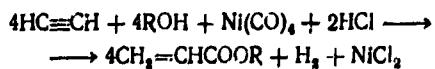
This method is studied in greater detail in the description of methods of production of acrylic acid.

2. From ethylene oxide and prussic acid in the presence of basic type catalysts:

$$H_2C{-\!\!-\!\!-}CH_2 + HCN \longrightarrow HOCH_2CH_2CN$$
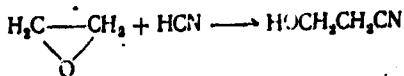
The ethylene cyanohydrin produced as an intermediate product is hydrolyzed and esterefied in one stage, producing acrylic acid ester:

$$HOCH_2CH_2CN + H_2SO_4 + ROH \longrightarrow CH_2{=}CHCOOR + NH_4HSO_4$$
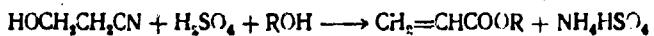
This method is less economical than the first method.

3. From ketene or formaldehyde in the presence of aluminum chloride:

$$CH_2{=}C{=}O \longrightarrow CH_2{-}C{=}O \xrightarrow{ROH} CH_2{=}CHCOOR + H_2O \qquad CH_2{-}CH_2$$
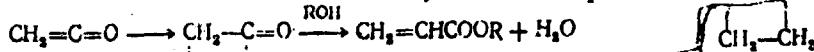
At room temperature, β-propiolactone is formed as an intermediate product.

4. From acrylonitrile:

$$CH_2{=}CHCN + H_2SO_4 + ROH \longrightarrow CH_2{=}CHCOOR + NH_4HSO_4$$
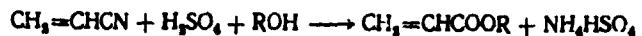
Alkyl methacrylates are produced industrially either by a continuous method from acetone and prussic acid through acetone cy   ron in the presence of basic catalysts·

$$\begin{matrix} H_3C \\ \\ H_3C \end{matrix}\!\!\!\!\!\!>\!\!C{=}O + HCN \longrightarrow \begin{matrix} H_3C \\ \\ H_3C \end{matrix}\!\!\!\!\!\!>\!\!C\!\!<\!\!\begin{matrix} OH \\ \\ CN \end{matrix}$$

$$\begin{matrix} H_3C \\ \\ H_3C \end{matrix}\!\!\!\!\!\!>\!\!C\!\!<\!\!\begin{matrix} OH \\ \\ CN \end{matrix} + H_2SO_4 + ROH \longrightarrow CH_2{=}C{-}COOR + NH_4HSO_4$$
$$\underset{CH_3}{|}$$
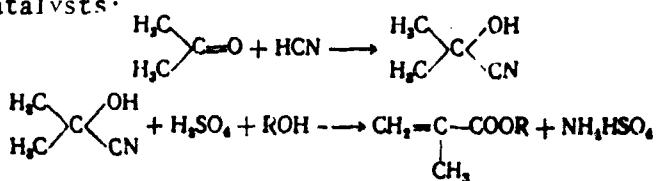
or by a continuous method from isobutylene and oxides of nitrogen through α-oxyisobuteric acid:

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$$CH_3-C=CH_2 \xrightarrow{N_2O_4} CH_3-C-COOH \longrightarrow$$
$$\underset{CH_3}{|} \qquad \underset{HO}{} \quad \underset{CH_3}{}$$

$$\longrightarrow CH_2=C-COOH \xrightarrow{ROH} CH_2=C-COOR$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$
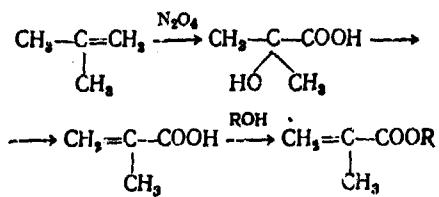
This last method is of great interest and is quite promising, since it utilizes readily available raw materials. The cost of monomers produced by this method is less than half the cost of monomers produced by the method involving acetone cynohydren [1]. The higher esters of acrylic and methacrylic acids are synthesized also by reesterification of the lower esters, primarily the methyl esters.

The pure monomers have a tendency toward spontaneous polymerization; therefore, they are stabilized with hydroquinone, the monomethyl ester of hydroquinone, phenothiazine and other radical polymerization inhibitors. Before use, the innibitor is removed from the monomer by fractional distillation; hydroquinone is removed by washing with a 5-10% solution cf alkali with subsequent drying with anhydrous sodium sulfate. The assortment of esters produced is great, and therefore they are used to produce film-forming agents with various physical and mechanical properties.

Butadiene is a colorless gas with a specific, sweet smell, easily soluble in ether, benzene, carbon tetrachloride and chloroform.

At the present time, butadiene is industrially produced basically from petroleum raw material. The most common method is catalytic dehydrogenation of n-butane and n-butylenes. A less common but very promising method of production cf butadiene is by high temperature thermal cracking of petroleum fractions. Sometimes butadiene is produced from ethyl alcohol [2], this is economically less suitable than the processes based on conversion of hydrocarbons, but the construction of plants for the production of butadiene from ethyl alcohol is less expensive.

Vinyl acetate is a colorless, strong smelling liquid, which mixes well with most organic solvents and to a limited extent with water.

Vinyl acetate is produced industrially from acetylene and acetic acid in vapor phase. Recently, a new method was developed for the production of vinyl acetate from ethyl and acetic acid both in liquid and in vapor phase. This method will apparently be widely used in industry.

Vinyladene chloride is a colorless liquid, which mixes well with many organic solvents. It is produced industrially primarily by dehydrochlorination of 1, 1, 2-trichloroethane in the presence of calcium oxide at 100°C. It has been reported in the literature [5] that vinyladine chloride is produced industrially by pyrolysis of trichloroethylene, but this method has not yet become widely used due to the difficulties of separating pyrolysis products which boil at nearly the same temperature.

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Table 5.1. Physical Properties of Basic Monomers used in the Synthesis of Polymerization Film Formers

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Monomer	m.p. °C	B.P. °C	Density d_4^{20}	Refractive index n_D^{20}	Water solubility, wt %	Heat of polymerization, kcal/mol (kJ/mol)
1,3-Butadiene	−108,9	−4,41	0,646 (0 °C)	1,4293 (−25 °C)	0,22 (0 °C)	17,3 (72,5)
Vinyl acetate	−84,0	73,0	0,9342	1,3958	2,5	21,3 (89,2)
Vinylidene chloride	−122,1	31,7	1,2122	1,4244	—	14,4 (60,3)
Vinyl chloride	−159,7	−13,9	—	1,33 (15 °C)	—	22,0 (92,2)
Styrene chloroprene	−30,6	145,2	0,9060	1,5439 (25 °C)	0,0125	16,5 (69,2)
n-Butyl acrylate	—	59,4	0,958	1,4583	—	16,2 (67,8)
n-Butyl methacrylate	−34,5	140,0	0,8998	1,4190	0,32	
Methyl acrylate	−76	164	0,8936	1,4215 (25 °C)	0,0027	13,5 (56,6)
Methyl methacrylate	−76	80,0	0,9535	1,4040	5,48	18,7 (78,4)
n-Octyl methacrylate	−48,2	100,3	0,9360	1,4130	1,50	13,0 (54,5)
n-Propyl methacrylate	—	105 (5 мм)	0,8890	1,4?90	—	—
Ethyl acrylate	—	141	0,9004	1,4200 (15,6 °C)	—	—
2-Ethylhexyl methacrylate	−72	99,5	0,9234	1,4068	1,5	—
	−90	213	0,8852	1,4349	—	—
Ethyl methacrylate	−75	117	0,9120	1,4115 (25 °C)	—	—

Vinyl chloride is a gas with a present odor, easily soluble in organic solvents and slightly soluble in water.

Vinyl chloride is produced industrially from ethylene, acetylene and ethane [6]. The easiest method of production of vinyl chloride is from ethylene by chlorination with subsequent dehydrochlorination of the dichloroethane formed by pyrolysis [7] or saponification. At the present time, gas phase (at 150-200°C) on liquid phase (at 20-30°C) hydrochlorination of acetylene is widely used for the synthesis of vinyl chloride. The production of vinyl chloride from mixtures of dilute gases containing acetylene and ethylene is quite promising [8]. In the USSR, vinyl chloride is produced both by saponification of dichloroethane, and by hydrochlorination of acetylene. The latter method is more convenient, since it forms a purer product. In Western Europe and in the USA, the method of gas phase hydrochlorination of acetylene is most popular.

Styrene is a colorless, transparent liquid with a specific odor, mixes well with many organic solvents. Of the many known methods of production of styrene, dehydrogenation of ethylbenzene is the most commonly used industrially.

Styrene is used for production of coatings of high hardness but low elasticity, unstable to the effects of water and various chemical reagents. Chloroprene is a colorless, transparent liquid which mixes well with all organic solvents and poorly with water.

Chloroprene is produced industrially by condensation of acetylene at 50-90%C with subsequent hydrochlorination of the monovinyl acetylene produced.

The physical properties of the basic monomers indicated above and others used for the production of film formers are shown in Table 5.1.

Modifying Monomers

Acrylic acid is a colorless, transparent liquid with a sharp odor, which mixes well with acetone, benzene, chloroform, ethynol, ether and water. It boils at 141°C and melts at 13.06°C. Its density is 20°C is 1.0511 g/cm^3, its refractive index is 1.4224. The heat of polymerization is 77,600 j/mol (18.5 kcal/mol). Acrylic acid is produced primarily by a modified Reppe method: from carbon monoxide, acetylene and water. These reagents, together with tetrahydrofuran and a small quantity of nickle chloride, are fed continuously into a reactor at a gauge pressure of 50 atm at 200°C. The unreacted acetylene, carbon monoxide and tetrahydrofuran are separated from the mixture produced, the tetrahydrofuran is recirculated, and the remaining acrylic acid is extracted and distilled. The most promising method of production of acrylic acid is vapor-phase oxidation of propylene [9] in the presence of solid catalysts such as oxides or salts of molybdenum, tellurium [10], manganese and nickel [11] with the formation of acrolein as an intermediate product. Acrylic acid is extracted from the vapor phase by condensation of absorption in scrubbers.

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Comparatively recently, acrylic acid has been produced by hydrolysis of acrylonitrile, as a result of the significant reduction in the cost of acrylonitrile. Hydrolysis of acrylonitrile is performed in the presence of an excess of sulfuric acid (2 kg per kg acrylic acid).

It is also possible to produce acrylic acid from ethylene through ethylene cynohydron, from acrylein [12, 13], β-halide propionic acids, etc.

Due to the great tendency of acrylic acid toward spontaneous polymerization, it is stored only in the presence of effective inhibitors such as anhydrous halides of arsenic, tin, antimony and bismuth; various salts of metals dissolved in the monomer; as well as methylene blue, di-β-naphthene and copper powder.

Methacrylic acid is a colorless liquid, easily soluble in alcohol, ether and water. It boils at 161°C and melts at 16°C. Its density of 20°C is 1.0153 g/cm^3, its index of refraction is 1.4314. The heat of polymerization is 66,250 j/mol (15.8 kcal/mol).

It is produced industrially from acetone cynohydron, which is first converted to the amide by sulfuric acid at 130-140°C, then hydrolyzed.

Like acrylic acid, methacrylic acid can be stored only in the presence of polymerization inhibitors.

Acrylonitrile is a colorless, transparent, poisonous liquid, which mixes with most organic solvents. It boils at 77.3°C and melts at 82°C [sic -- tr]. Its density at 20°C ir 0.8060 g/cm^3, its index of refraction is 1.3911. The heat of polymerizati n is 72500 j/mol (17.3 kcal/mol).

Acrylonitrile is produced industrially basically from ethylene oxide and prussic acid through ethylene cynohydron. The dehydration catalyst of ethylene cynohydron are the formiates of the alkali or alkali-earth metals.

Direct synthesis of acrylonitrile from prussic acid and acetylene is common [14], but requires highly pure acetylene.

Recently [15, 16], a more economical single-stage method of production of acrylonitrile has been developed -- oxidation of propylene in the presence of ammonia and catalysts: molybdenum and phosphorous-molybdenum salts of tin, antimony and bismuth.

Acrylonitrile, like acrylic and methacrylic acids, can be stored only in the presence of polymerization inhibitors, most frequently hydroquinone, pyrogallol and amines.

The amide derivatives of unsaturated acids are widely used for the production of thermo reactive film formers.

Acrylic and methacrylic acid amides are most frequently used. Recently, the attention of paint and varnish workers has been attracted by methylol amides, which are produced by the interaction of amides with formaldehyde:

$$H_2C=C-CONH_2 + CH_2O \longrightarrow H_2C=C-CONHCH_2OH$$
$$\hspace{1.5cm} | \hspace{5cm} |$$
$$\hspace{1.5cm} R \hspace{5cm} R$$
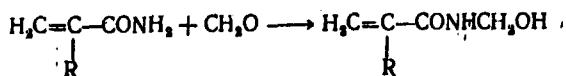
This reaction occurs readily in an alkaline medium at pH 9-10 at a temperature of around 60°C [17]. In the case of methylolation in an acid medium, methylol amides can be condensed to form methylene-bis-amides:

$$2H_2C=C-C-NHCH_2OH \longrightarrow$$
$$\hspace{1cm} | \hspace{0.3cm} ||$$
$$\hspace{1cm} R \hspace{0.3cm} O$$

$$\longrightarrow H_2C=C-C-NHCH_2OCH_2HN-C-C=CH_2 + H_2O$$
$$\hspace{1cm} | \hspace{0.3cm} || \hspace{3cm} || \hspace{0.3cm} |$$
$$\hspace{1cm} R \hspace{0.3cm} O \hspace{3cm} O \hspace{0.3cm} R$$
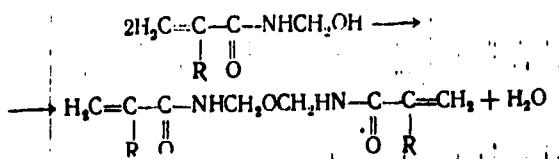
The amides and methylol amides of acrylic and methacrylic acid are white crystalline products. The melting points of the most frequently used amide derivatives are presented below (in °C):

Acrylamide	84-86
Diacetone acrylamide	52-53
Methacrylamide	107-108
Methylolacrylamide	73-74
Methylolmethacrylamide	53-55

Diacetone acrylamide has been synthesized relatively recently [18] by the interaction of acetone and acrylonitrile in the presence of sulfuric acid. It is easily soluble in benzene, acetone, ethyl acetate, water and copolymerizes easily with other acrylic monomers.

Jedlinsky and Paprotny [19] have synthesized a number of alkylolacrylamides (Table 5.2) by the interaction of amino alcohols with acrylic and methacrylic acid chlorides in acetonitrile:

$$R-COCl + 2HO-R_1NH_2 \longrightarrow R-CONH-R_1OH + HOR_1NH_2 \cdot HCl$$
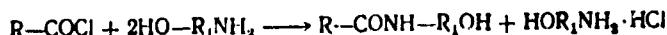
Table 5.2. Physical Properties of Certain Alkylolacrylamides.

Monomers	M. P. °C	B. P. °C	Index of Refraction n_d^{20}
2-acrylamide-1-butanol	-	120(0.04 mm Hg)	1,4955
2-acrylamide-2-methyl-1-propanol	83.5-84.5	-	-
2-acrylamide-2-oxymethyl-1,3-propanediol	131-133	-	-
2-methacrylamide-1-butynol	40-42	130-135(0.3 mm Hg)	1,4918
2-methacrylamide-2-methyl-1,3-propanediol	102-103	-	-

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All of these chemicals polymerize easily under the influence of free radical initiators.

Monomers containing hydroxyl groups are of doubtless interest for the production of thermosetting film formers. These monomers include acrylic and methacrylic oxyesters, produced by interaction of the acids with epoxy compounds in the presence of catalysts such as bases, sulfoxides [20], thioesters [21], chromium hydrochlorides [22], etc.

The physical properties of the most common hydroxyl-containing acrylic acid esters are presented in table 5.3.

Monomers containing epoxy groups are also used for the production of thermosetting film formers. They are synthesized primarily of epichloro-hydrin and the salts of unsaturated acids. Data have been presented in the literature on the industrial production of glycidyl methacrylate.

Table 5.3. Physical Properties of Acrylic Oxyesters

Monomer	BP, °C	Density, d_4^{20}	Index of Refraction n_d^{20}
2-Oxyethylacrylate	82 (5mm Hg)	1,1038	1,4505
2-Oxyethylmethacrylate	95 (10mm Hg)	1,077	1,4510
Oxypropylacrylate	75 (5mm Hg)	1,056	1,4448
Oxypropylmethacrylate	96 (10 mm Hg)	1,027	1,4460

The physical properties of glycidyl esters of certain unsaturated acids are presented in Table 5.4.

Table 5.4. Physical Properties of Glycidyl esters of unsaturated acids.

Monomer	BP, °C	Density, d_4^{20}	Index of Refraction n_d^{20}
Glycidylacrylate	57 (2 mm Hg)	1,1074	1,4495
Glycidylmethacrylate	65 (4 mm Hg)	1,0728	1,4505
Methylglycidylitaconate	108 (mm Hg)	1,1860	1,4632

Monomers in this group also include allyl glycidyl ester, butadiene monoxide and vinyl cyclohexane. One significant shortcoming of all epoxy monomers is their high toxcity, limiting their use in the production of film formers.

Amino alkyl unsaturated acid esters fall in the class of modifying monomers used in the synthesis of polymer film formers. Of the methods of production of tert-amino esters described in the literature, the most common is reesterification of lower alkyl esters of unsaturated acids (acrylic, methacrylic, fumaric) with amino alcohols [24, 25] and asalination of the amino alcohols with unsaturated acid chlorides. The method of direct esterifica-tion [26-28] is used to a much lesser extent, which is explained by the necessity of using high temperatures for dissociation of the salt formed.

These compounds can be produced by acylation of amino alcohols with halide propionic acid halides [29].

Other methods of synthesis of tert-aminoesters of unsaturated acids are also known [30]. Industrial production of certain tert-aminoesters has been reported [27].

There is considerable interest in acrylic and methacrylic acid esters with primary and secondary amino groups in the alcoxy [31].

The physical properties of some of the most typical tert-aminoalkyl unsaturated acid esters are presented in Table 5.5.

Table 5.5. Physical properties of tert-aminoalkyl unsaturated acid esters

Monomer	BP, °C	Density, d_4^{20}	Index of Refraction n_d^{20}
Bis-(2-diethyl amino ethyl fumarate)	155 (1 mm Hg)	0.9930	1,4660
Dimethyl amino ethyl acrylate	61.5 (13 mm Hg)	0.9406	1,4370
Dimethyl amino ethyl methacrylate	65.5 (8 mm Hg)	0.9321	1,4395
Diethyl amino ethyl methacrylate	89.0 (9 mm Hg)	0.9206	1,4445
Diethyl amino ethyl acrylate	70 (6 mm Hg)	0.9248	1,4425
tert-butyl amino ethyl methacrylate	90-95 (12 mm Hg)	0.9182	1,4420

The amino esters of α, β-unsaturated acids are low-toxcity products having, however, a poisoning effect on the skin and mucous membranes. The low volatility of these monomers practically eliminates the possibility of creation of toxic concentrations in the air.

The metal-containing monomers are of great interest for the synthesis of polymerization film formers having a number of valuable specific properties, in particular bactericidal properties.

The first representative of tin-containing acrylates, trimethyl acryloxy stannan, was produced by Anderson [32] by the reaction of hexaethyl stannoxide with methylmethacrylate:

$$(C_2H_5)_3SnOSn(C_2H_5)_3 + 2CH_2\!\!=\!\!C\!\!-\!\!\underset{O}{\overset{O}{C}}\!\!-\!\!OCH_3 \longrightarrow$$
$$\longrightarrow 2(C_2H_5)_3SnOC\!\!-\!\!C\!\!=\!\!CH_2 + CH_3OCH_3$$
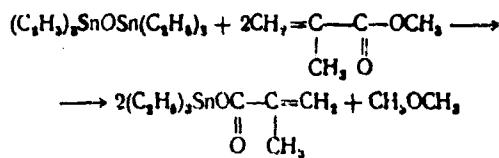
Koton et al. [33] first synthesized the methacrylates of trimethyl-, triethyl-, tributyl and triphenyltin by the interaction of the corresponding trialkyl-(aryl)-tin oxide hydrates and methacrylic acid in an acetone solution and described their properties. Acrylates and methacrylates containing atoms of lead [34-36], mercury [34], antimony [37] and germanium [38] have also been synthesized. The melting point of certain metal-containing acrylates and methacrylates are presented in Table 5.6.

Table 5.6. Properties of Certain Metal Containing Acrylates and Methacrylates

Monomer	BP°C	Biblio Ref
Dibutyldimethacryloxystannan	50-52	39
Trimethylmethacryloxystanan	122	33
Triethylmethacryloxystanan	76-79, 75	33 - 40
Tributylmethacryloxystanan	20-22, 17	33 - 40
Dimethyldimethacryloxystanan	141	40
Triphenylmethacryloxystanan	91-92	33
Diphenyldimethyloxyplumban	225	35
Diphenylstibylmethacrylate	113-115	37

Relative Activities of Monomers

In order to calculate the composition of a copolymer, it is necessary to know the relative activity (r) of monomers used in copolymerization, i. e., the ratio of the rate constance of the interaction of the monomer $[M_1]$ and the similar radical to the rate constance of interaction of the same monomer with a second radical.

Table 5.7. Copolymerization Constants for Various Pairs of Monomers

Monomers		Copolymerization Constants		Temperature °C	Biblio Ref
M_1	M_2	r_1	r_2		
Acrylic acid	Acrylomide	0.36	1.38	60	41
	Acrylonitrile	1.15	0.35	50	42
	Vinylacetate	2.0	0.1	70	43
	Vinylchloride	8.2	0.027	40	44
	Methylmethacrylate	0.225	1.25	70	45
Acrylonitrile	Butadiene	0.0	0.35	50	46
	Vinylacetate	6.0	0.02	60	47
	Vinylidenechloride	0.91	0.37	60	48
	Vinylchloride	3.28	0.02	60	49
	Vinylchloride	4.2	0.04	38	50
	Chloroprene	0.01	6.07	50	46
Butylacrylates	Ethylacrylate	0.44	0.95	80	51
	Acrylonitrile	1.005	1.003	60	52
	Acrylonitrile	0.89	1.2	60	53
	Butadiene	0.08	0.99	5	54
	Vinylchloride	4.4	0.07	45	55
Butylmethacrylate	Acrylonitrile	1.08	0.31	60	56
	Vinylacetate	28.8	0.023	60	56
	Vinylidenechloride	2.2	0.35	68	57
	Vinylchloride	13.5	0.05	45	58
	Glycidylmethacrylate	0.79	0.94	-	59
Vinylacetate	Vinyl	0.1	6.0	68	57
	Vinylchloride	0.3	2.1	68	57
	Vinylchloride	0.23	1.68	60	58
Vinylchloride	Butadiene	0.055	8.8	50	60
	Vinylidenechloride	0.21	3.15	53	61
Glycidylmethacrylates	Acrylonitrile	1.32	0.14	60	62
	Vinylacetate	4.60	0.055	60	63
	Vinylchloride	2.30	0.30	70	64
	Vinylchloride	8.84	0.04	70	65
Methacrylamide	Acrylonitrile	1.26	0.67	60	66
	Acrylonitrile	0.95	1.4	60	53
	Butadiene	0.05	0.76	5	54
	Vinylacetate	9.0	0.1	60	67
	Vinylacetate	6.7	0.029	50	68
	Vinylidenechloride	0.60	0.85	60	69
	Vinylchloride	4.4	0.12	50	70
	Vinylchloride	4.0	0.06	45	55
	Chloroprene	0.078	13.1	60	71
Methacrylic acid	Butadiene	0.526	0.201	50	72
	n-butylmethacrylate	0.53	1.11	-	59
	Vinylacetate	20.0	0.01	70	43
	Vinylidenechloride	3.0	0.15	70	73
	Vinylchloride	0.36	0.025	40	44
Methacrylic acid	Glycidylmethacrylate	0.85	1.18	-	59
	Diethylaminoethyl-methacrylate	0.98	0.90	70	74
	Methacrylamide	2.0	0.3	70	75

Table 5.7. Continued

Monomers		Copolymerization Constants		Temperature °C	Biblio Ref
M_1	M_2	r_1	r_2		
Methylmethacrylate	Acrylonitrile	1.35	0.18	60	46
	Butadiene	0.25	0.75	90	49
	Butadiene	0.32	0.70	-	76
	n-butylmetha-crylate	1.22	0.76	-	77
	Vinylacetate	20	0.015	60	58
	Vinylidenechloride	2.53	0.24	60	48
	Vinylchloride	10	0.1	70	57
	Glycidylmeth-acrylate	0.75	0.94	60	78
	Glycidylmeth-acrylate	0.76	0.88	-	79
	Ethylacrylate	2.0	0.28	-	80
	Ethylmethacrylate	0.99	0.40	-	77
Styrene	Acrylic acid	0.15	0.25	60	81
	Acrylonitrile	0.41	0.04	60	48
	Butadiene	0.78	1.39	60	49
	Butadiene	0.23	1.48	50	46
	n-butylmetha-crylate	0.56	0.40	60	82
	Vinylidene-chloride	1.85	0.085	60	83
	Vinylchloride	17	0.02	60	83
	Vinylchloride	35	0.067	50	84
	Glycidylmeth-acrylate	0.50	0.60	120	85
	Glycidylmeth-acrylate	0.45	0.55	60	62
	Glycidylmeth-acrylate	0.34	0.63	-	86
	Methacrylic acid	0.15	0.7	60	81
	Methylacrylate	0.76	0.26	60	87
	Methylmeth-acrylate	0.52	0.46	60	49
	Chloroprene	0.05	7	70	88
	Ethylacrylate	0.77	0.13	60	87
	Ethylmethacrylate	0.53	0.41	60	82

When we know the copolymerization constants, we can calculate the compositions of copolymers using the formula

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]}$$

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where $[M_1]$ and $[M_2]$ are the molar concentrations of monomers M_1 and M_2; r_1 and r_2 are the copolymerization constants for monomers M_1 and M_2.

The copolymerization constants are determined experimentally for each pair of monomers or calculated on the basis of the Q, e plan suggested by Alfrey and Price, using the formulas

$$r_1 = \frac{Q_1}{Q_2} \exp[-e_1(e_1 - e_2)]$$

$$r_2 = \frac{Q_2}{Q_1} \exp[-e_2(e_2 - e_1)]$$

where Q is a term characterizing resonance stabilization;
e is a term characterizing polarization of the monomer.

The values of copolymerization constants for most monomers used for the synthesis of polymerization film formers are presented in Table 5.7. They were produced by quantitative determination of the composition of copolymers with various ratios of monomers in the initial mixture.

Table 5.8. Values of Q and e for certain Monomers.

Monomer	e	Q
Butadiene		
Styrene		
2-vinylpyradiene		
n-octylmethacrylate		
Methacrylane	$-1,05$	2,39
n-butylmethacrylate	$(-0,80)$	$(1,00)$
Vinylacetate	$-0,50$	1,30
n-hexylmethacrylate	$-0,31$	0,78
Glycidylmethacrylate	$-0,26$	1,70
Ethylmethacrylate	$-0,23$	0,72
Vinylchloride	$-0,22$	0,026
Ethylacrylate	$-0,12$	0,70
Vinylidenechloride	$-0,02$	0,78
Methylmethacrylate	$0,17$	0,56
Dimethylacrylate	0,20	0,044
Ethyleneglycol	0,22	0,52
Diethylaminoethyl-	0,36	0,22
methacrylate	0,40	0,74
Stearylmethacrylate	0,42	1,08
Methylacrylate	0,42	2,08
Methacrylic acid	0,56	1,07
Acrolane	0,60	0,73
Acrylic Acid	0,65	2,54
Methacrylonitrile	0,73	0,85
Butylacrylate	0,77	1,15
Acrylonitrile	0,81	1,12
Methacrylamide	1,06	0,51
Acrylamide	1,20	0,60
Maleic anhydride	1,24	1,46
	1,30	1,18
	2,25	0,23

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The values of Q and e for calculation of copolymerization constants using the formulas suggested by Alfree and Price are presented in Table 5.8.

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CHAPTER VI

PAINT AND VARNISH MATERIALS

Paint and varnish materials are complex, multicomponent systems. In addition to the basic components -- film former and pigment -- they include other ingredients: solvents, hardeners, catalysts, fillers, plasticizers, thickerners, compounds preventing the development of bacteria, etc.

The necessity of introducing various additives depends both on the method of production of the film former, and on its properties. For example, coalescing additives, thickerners, antifoaming agents and protective colloids are frequently added to latex paints, while various buffer materials are frequently added to water-soluble paints to maintain the required pH of the medium.

Paint and varnish materials based on thermoplastic film formers form coatings as a result of evaporation of the solvent. One shortcoming of all thermoplastic film formers is their low resistance to the effects of solvents and high temperatures.

The introduction of react e comonomers to a polymerizing system converts the thermoplastic copolymers to thermoreactive products. This introduction of a cross-linking group to a polymer chain was patented by Strein in 1939 [1].

One interesting and promising class of thermosetting polymerization resins, suitable for use as paint and varnish materials and coatings, consists of the thermoreactive acrylic resins. They include the copolymers of acrylic and methacrylic acid alkyl esters, which contain reactive groups, with various vinylic monomers.

Thermosetting acrylic resins are usually produced of three or more monomers. One gives the films hardness (methylmethacrylate, styrene, vinyltoulene, acrylonitrile), another gives them elasticity (ethylacrylate, 2-ethyl hexyl acrylate), a third facilitates the formation of a reticular

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structure (acrylamides, methylol acrylomides, oxyalkyl acrylates, unsaturated
acids or their anhydrides, monoacrylic glycol esters, unsaturated acid deriva-
tives containing epoxy, amine and other groups). The monomers most frequently
used for the production of thermosetting acrylic resins, and the properties
which they give film formers and coatings are listed below:

Acrylic acids ⎫
Maleic anhydrides⎭   Hardening Catalysts

Acrylomide ⎫
Acrylic acids ⎪
Butoxymethacrylamide ⎬   Hardenability
Blycidyl methacrylate ⎪
Oxyalkyl acrylates ⎭

Acrylonitrile ⎫
Vinyltoulene ⎪
Methylmethacrylate ⎬   Hardness
Styrene ⎭

Butylacrylate ⎫
Butylmellate ⎪
Ethylacrylate ⎬   Elasticity
2-ethylhexylacrylate⎭

The most common monomer used to give coatings hardness is styrene [2-5].
As the styrene content of a copolymer increases, in addition to increasing
hardness, the resistance to water and various chemical reagents increases,
but the compatibility of the copolymer with aminoresins and the light resistance
of the coating decrease. Styrene and vinyl toulene derivatives are also used
to give coatings hardness. The use of acrylonitrile for this purpose [8] in-
volves certain difficulties, resulting from the poor solubility and high viscosity
of the copolymer solutions. However, it has been reported [9] that the hydro-
lysis of acrylic polymers containing acrylonitrile can result in the formation
of amide groups in the side chains of the polymer.

The esters of acrylic and methacrylic acids give coatings resistance to
atmospheric effects and durability [10-13], while acrylic acid esters, further-
more, give coatings elasticity, and the esters of methacrylic acid increase
the hardness and resistance to the effects of chemical reagents [14].

Thermosetting acrylic resins are classified on the basis of the functional
groups included in their composition. Some types of resins contain several
functional groups at the same time. Thermosetting acrylic resins are hardened
either by the introduction of a cross-linking agent (hardener) or as a result
of the interaction of the functional groups contained in the macromolecules of
the resin itself. The most common functional groups in thermosetting acrylic
resins and the hardners used with them are presented below [15]:

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Carboxyl	Glycols Diisocyanates Melamine resins Urea resins Phenol resins Epoxy resins
Hydroxyl	Dibasic acids Dialdahydes Diisocyanates Melamine resins Urea resins Epoxy resins
Methylolamide	Diisocyanates Melamine resins Urea resins Phenol resins Epoxy resins
Epoxy	Acid Anhydrides Amines Diisocyanates Acids Methylolamides Polyamides

Acid type monomers such as acrylic, methacrylic, itaconic and maleic acids, maleic anhydride and others are used not only as hardeners but also as internal catalysts to reduce the hardening point of certain types of resins [2, 10, 16-20], to increase the adhesion to various substrates [2, 10-12, 18-20], and to improve compatibility with other resins.

Chlorene-containing vinylic monomers and simple vinylic esters are also used in thermosetting acrylic compositions [21-22], however, they have very low reactivity for copolymerization with acrylates (see Chapter 5); therefore, the copolymers produced are inhomogeneous in composition.

Thermosetting resins based on copolymers of alkyl acrylates and their derivatives with olefins, primarily with ethylene [23-27], are somewhat more frequently used.

In order to increase the hardness and adhesion of coatings, it has been suggested [28] that acrylic monomers be used, containing both amine and amide groups (aminoamides). The protective and adhesion properties are improved by introduction of unsaturated acids [29-35] or their salts [36-39] to the composition of aminoalkylester resins.

Various specific properties of coatings are achieved by introduction of spiroacetals [40], 5-alkaline-m-dioxanyl acrylates [41], 3-(2-oxyalkyl)-oxazolidinon acrylates [42], n-acyl acryloxy alkanamides [43], as well as various acrylic monomers containing phosphate and phosphite rings [44], as well as carbamate groups [45] to the composition of the resins.

The wide selection of monomers for thermosetting resins allows the composition of the resins to be varied widely, producing coatings with various physical and mechanical properties.

Latex Paint and Varnish Materials

The use of latex polymers for the production of paint and varnish materials (latex paints) allows compositions to be used with high contents of dry matter at normal viscosity, even for polymers with molecular weights on the order of several million.

The latex paints include up to 25 different ingredients, playing defined roles in the process of preparation and usage [46-53]. In addition to pigments and fillers, the ordinary components of any paint system, latex paints include certain specific additives. These include protective colloids and thickeners, coalescing additives, anticorrosion agents, fungicides, as well as materials increasing the cold resistance of the latex.

The most commonly used white pigments for latex paints are titanium dioxide in the rutile or anatase form [54, 55]. Zinc oxide is used less frequently, since it may reduce the stability of the emulsion system [56]. Stabilized aqueous dispersions of colored pigments are prepared separately and added to the latex paints to color them. Various iron oxide pigments are used in the manufacture of latex paints. The most commonly used filler for latex paints of various types is talc [57].

The use of water-soluble polymers for stabilization and thickening of latex materials helps to disperse the pigment in the aqueous phase, protects the paint from coagulation and settling and allows viscosity to be regulated. Commonly used stabilizers include cellulose, starch, caseinates and other polymers which prevent the coalescence of latex particles as they are brought together by various factors. Thickeners increase the overall viscosity of the system, thus increasing its stability [58-67]. Sometimes, this type of compound is added directly during the polymerization process, facilitating an increase in the stability of the latex formed [68].

The coalescing additives (carbitol, carbitol acetate, acetate butyl cellosolve, etc.) assure good meshing of the particles during the process of formation of the coating [60]. Furthermore, they help to form a shiny coating with good adhesion and good resistance to the effects of washing agents.

Anticorrosive agents (for example, sodium benzoate) prevent the corrosion of metal surfaces, particularly of the containers used to transport water-emulsion paints.

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Fungicides and protective substances (such as sodium pentachlorophenolate) are used to protect the paint and varnish materials and coatings from micro-organisms.

Additives increasing cold resistance (hydrozene, fatty amine derivatives, guanidine salts) prevent coagulation of the latex particles at low temperatures during transportation and storage in cold weather; the mechanism of their action is complex and is explained by various factors in different works, al-through most authors believe that the action of the additives is related to reduced freezing of the aqueous phase and a reduction in the number of needle-shaped ice crystals, which break down the protective material interlayers [69-71].

To produce pigmented latex materials (paints), a pigment paste is first prepared, to which the thickeners are added with a minimum quantity of water. The remaining additives are introduced, generally, to the pigment paste or following mixing of the pigment paste with the latex.

Recently, a method has been described in the foreign patent literature for production of ready-to- use latex paint in the process of aqueous-phase polymerization of acrylic, vinyl acetate and bivinyl-styrene monomers [72-74]. In this case the pigments (titanium dioxide or zinc oxide), fillers, pigment dispersers, thickeners and other ingredients are introduced to the monomer mixture during polymerization, producing a finished white paint which forms a smooth, shiny coating with high wear resistance. The selection of the corresponding emulsifiers and protective colloids is particularly important in this case; they must provide stability of the complex, multicomponent dispersed system. Most commonly used is a mixture of protective colloids with ionic and nonionogenic emulsifiers such as cellulose derivatives, dode-cyl benzyl sulfonates, polyethylene glycol laurates and other compounds.

Thus, we can state that progress in the area of utilization of polymer dispersions for coatings, in particular for the preparation of water-diluted paint, depends on the synthesis and application of new materials, such as emulsifiers, thickeners, stabilizers, coalescing and other special additives. This problem, together with the creation of new polymer binders, has been the subject of many studies in recent years [60, 75, 76].

A latex paint can be thought of as a dispersion of pigments and fillers in a binder. In this sort of system, when the particles of both dispersed phases interact in the liquid dispersion medium, a disordered 3-dimensional network called a coagulation structure [77-83] arises, preventing the separa-tion of individual paint components, in particular the precipitation of the pigment. However, the structure must not be too strong, so as not to hinder application of the material to the surface. Therefore, a thixotropic paint, in which the structure can reversibly regain its initial strength following breakdown, is particularly valuable. This is achieved by adding materials giving the paints thixotropic properties [84], for example, complex-forming titanium compounds [85].

Many polymer dispersions and latexes are used as film-forming materials for latex paints. Their selection is determined by the purpose of the material, as well as the level of production, availability of raw material and other economic considerations. For example, in Japan, binders are most commonly based on polyvinyl acetate [86-88], while in the USA acrylate polymers and copolymers are also becoming increasingly popular [89-92].

Materials based on bivinyl-styrene latex are still quite widely produced; for example, in the USA they represent 27% of all latex paints produced.

Like other paint and varnish materials, latex paints, depending on the nature of the film former and the presence of functional groups, are divided into thermoplastic and thermosetting.

Thermoplastic Paint and Varnish Materials Based on Latex Film Formers

Paint and varnish materials based on bivinyl-styrene latex. Bivinyl-styrene latex was the first film former used for the production of latex paints. It continues to be significant in this area [60,93]. These latex can be looked upon as polystyrene latexes, in which bivinyl is used for internal plastification [94]. Bivinylstyrene latexes are being widely replaced by polystyrene latexes [95], plasticized following polymerization [96].

Many studies have shown that a change in the ratio of styrene to bivinyl strongly changes the properties of these coatings [94, 97-99]. For example, an increase in the content of bivinyl causes a decrease in the hardness of the coating; as the quantity of styrene increases, the minimum film-formation temperature increases. Latexes with styrene: bivinyl ratios of 65, 35 to 55: 45 are usually used.

Bivinyl styrene latex paints can be used on plaster, cement and asbestos-cement slabs, concrete, stone, plastics, ordinary and klinker brick, Lincrust, wood, plywood, etc. In contrast to oil-base paints, latex paints can be applied to moist surfaces [101]. Due to their satisfactory adhesion to various surfaces and good decorative properties, bivinyl styrene latexes can be used as pore fillers, primers, and also as covering layers [52]. Bivinyl styrene latexes have greater resistance to freezing and thawing than other polymer dispersions and provide high water resistance as well as saponification resistance. Coatings based on bivinyl styrene latexes can be washed with soap and water; they do not take up greasy dirt, which is easily washed off. For this reason, bivinyl styrene latex paints are recommended for internal finishing of rooms in which cleanliness is important -- bathrooms, kitchens, nurseries, etc. [102, 97].

The shortcomings of bivinyl styrene paints included the formation of foam during manufacture, requiring the introduction of significant quantities of antifoaming additives [46, 103]. Furthermore, coatings produced from bivinyl styrene latex are not highly resistant to the effects of ultraviolet light. This results from the presence in the polymer of unsaturated bonds and the possibility of chemical conversion by attachment of oxygen in the air

at the locations of these bonds, causing rapid aging of the coatings [104]. This shortcoming is the reason why coatings based on bivinyl styrene latexes were used for sometime only for internal room painting [105].

At the present time, bivinyl styrene latexes are being successfully used for exterior painting as well [97, 106]. This has resulted to a great extent from the modification of bivinyl styrene latexes with resins and oils [107], usually introduced to the latex as an emulsion or solution in an organic solvent. These modifiers may include alkyl, alkyd-phenol, alkyd-epoxy and other resins, allowing the spreading properties of the material to be improved, the pigment content to be increased and the adhesion of coatings to smooth surfaces to be increased. Various functional groups such as carboxyl, hydro-xile, nitrile and other groups are introduced to the latex polymer for the same purposes [108-110]. In addition to the fact that these gouprs improve the adhesion of the paint as a result of chemical interaction between adhesive and substrate [111-113], the stability of bivinyl styrene latexes is improved [114], viscosity increases, and the process of formation of the coating is accelerated [115]. All of this helps to improve the physical and mechanical properties of the coatings and increase their resistance to the effects of water [116].

One important area of application of bivinyl styrene latex film formers is the paper and printing industry. When used as coatings on paper [117, 118] together with such widely used film-forming materials as starch, casein, poly-vinylic alcohol, etc., the printing properties of paper are improved, as well as the quality of offset and letter press images and wear resistance of the printing both dry and particularly wet.

Recipes of special paint and varnish materials have been developed for the printing industry on the basis of SKS-30 latex with the addition of an aqueous solution of polyvinylic alcohol [119].

Paint and varnish materials based on polyvinyl acetate latexes are most broadly used in various branches of industry. Polyvinyl acetate dispersions, depending on the emulsifier used, may have colloidal-size particles, in which case they are called latexes, or particles with diameters of up to several microns. A dispersion with particles of large diameter, produced with a stabilizer such as polyvinylic alcohol, is called a polyvinyl acetate emulsion.

Coatings based on polyvinyl acetate emulsions are rather hard, have good adhesion to various substrates due to the presence of polar acetogroups in the polymer chain, have good shine, durability and resistance to washing agents.

One valuable property of polyvinyl acetate coatings is their high vapor permeability [120], facilitating the drying of wood and plaster after painting and formation of the coating.

The high adhesion of polyvinyl acetate is the reason that its emulsions make up a primary component part of primer base coat. The vinyl acetate is introduced as a basic product and also as a partially hydrolyzed, together with such compounds as colophony, mineral oil and pigments [118, 121-127].

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One of the advantages of the use of paints based on polyvinyl acetate emulsions is the ease of manufacture: in contrast to bivinyl styrene latexes, this emulsion can be produced directly in paint plants using the equipment for the synthesis of alkyd resins as is done in the USA [93].

Since polyvinyl acetate does not form an elastic film at ordinary temperatures, significant quantities of plasticizer are added to paint based on this product [128-150]. The plasticizers also increase the ability of the binder to coalesce and form film. Plasticizers are generally made of such compounds as dibutyl thalate, tricresyl phosphase and others. The addition of plast- cizers to polyvinyl acetate emulsions is performed gradually, with careful mixing of the system to avoid coagulation.

Plasticized polyvinyl acetate emulsions are broadly used for the manufacture of paints used for various purposes, particularly paints designed for construction work [56, 131-134]. However, the presence of the plasticizer results in sweating of the plasticizer from the coating; this increases the brittleness of the coating. Therefore, polyvinyl acetate emulsions, like bivinyl styrene latexes, were long recommended only for internal painting and for finishing of rigid surfaces [135].

The copolymerization of vinyl acetate with other monomers allows the shortcomings inherent in plasticized vinyl acetate homopolymers to be overcome, producing a stronger bond between plasticizer and basic film formers [134]. Currently, these copolymer binders are used in the manufacture of paints for external work, in particular for painting of building exteriors [107, 1034-140].

Among the copolymer vinyl acetate latexes used as binders for paints, we should note the copolymers of vinyl acetate with vinyl stearate, vinyl laurate [134], vinyl caproate [85], vinyl propionate, vinyl-and oxtyl mileates, and vinyl fumerate [135]. These film formers have low film formation temperature, and the coatings which they produce are sufficiently elastic without the introduction of a plasticizer.

New film formers have been produced [139, 141-144], consisting of co- polymers of vinyl acetate with vinylic esters of branch, synthetic fatty monobasic carboxylic acids. The best properties are those of a copolymer in which the component ratio is 1:1. The introduction of the vinylic ester of the branched acid allows the production of a material, the viscosity of which increases only slightly following repeated freezing and thawing [144]. This also increases the resistance of the latexes to mechanical actions, the wear resistance of coatings based on them and the resistance to the effects of water and alkalis [139].

Recently, copolymers of vinyl acetate with ethylene have been widely used: these copolymers have high flexibility and good technological properties [145-148]. Vinyl acetate-ethylene copolymer latexes are distinguished by their excellent pigment capacity and good coalesce at low temperatures; coatings produced from these emulsions have high adhesion and resistance to ultraviolet life. Paints based on them, due to their high alkali resistance, can be successfully used for external painting of brick walls as well as wood structures [148].

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Paint and varnish materials based on polyacrylate latexes. The best film formers are various polyacrylates -- polymers and copolymers of acrylic and methacrylic acid esters. Their broad utilization in industry was long hindered by the comparatively high cost of the initial monomers. However, currently acrylic polymers and copolymers, including latexes, occupy a leading position in the production of paint and varnish materials of various types, a result of the property of the coatings which they produce. Coatings based on polyalkyl acrylates are colorless, transparent, highly elastic; the glass point of lower polyalkyl acrylates is below room temperature and decreases with increasing molecular weight of the alkyl [149, 150]; the adhesion of polyalkyl acrylates is higher, the lower the softening temperature of the polymer.

One characteristic property of polyalkyl acrylate films is their high shine and atmosphere resistance, allowing such frequently encountered shortcomings of coatings as yellowing of films after exposure to light to be avoided.

Specially performed studies [151] have shown that coatings based on polymethyl acrylate and polyethyl acrylate did not change their color following three years testing on a roof, retained their initial shine and all physical and mechanical properties. Polyalkyl acrylate coatings have high resistance to the effects of ultraviolet rays, as well as mold, fungus, allowing them to be used for painting of products used under moist tropical climate conditions [152].

It must be noted that the use of polyalkyl acrylates (beginning with polyethyl acrylate) as film formers is difficult due to the great softness of the films which they form. For example, films of polymethyl acrylate of medium molecular weight have little tackyness and high relative elongation at rupture -- up to 1,000%; polyethyl acrylate films are even softer; polybutyl acrylate produces very tacky films at normal temperatures [147]. Copolymerization of acrylic acid esters with other monomers, particularly alkyl methacrylates, allows the valuable properties of polyalkyl acrylates to be used for coatings and produces films with a broad range of physical and mechanical properties.

Among the acrylic latexes most commonly used in the leather industry are latexes based on polymethyl acrylate, ethyl acrylate and their copolymers. They can be stabilized both with ordinary emulsifiers -- the salts of the sulfoacids [153, 154], and with emulsifiers of a new type [155], combining the properties of ordinary soaps -- salts of sulfurated acids -- with the properties of high molecular nonionogenic emulsifiers, widely used abroad under the trade name "Pluronic" [156]. The use of these emulsifiers for the production of polymethyl acrylate emulsions greatly simplifies the production and increases the stability of the latex [155].

Coatings made of latex based on polymethyl acrylate have high atmospheric resistance and elasticity over a broad temperature range [157], [158].

Among the acrylic latexes, copolymer latexes of acrylic and methacrylic acid esters are widely used, for example a methylacrylate-butylacrylate

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latex with a component ratio of 1:1. The introduction of small quantities of methacrylic acid or its amide to these copolymer latexes during polymerization increases the ability of the latexes and improves their film forming properties [159, 160]. These latexes are used for finishing of leather and the manufacture of construction paints.

A latex based on a copolymer of acrylate with vinylidene chloride [161] called Rhoplex A-9 (produced by Rohm and Haus) is widely used to coat paper. It is colorless, retains the flexibility of the paper, does not cause conglomeration, and can be easily colored. An ethyl acrylate-acrylonitrile copolymer with a component ratio of between 75:25 and 60:40 can also be used for the same purpose [162].

Acrylic latex paints are widely used in construction both for external and internal work, and frequently last 7 or 8 years [140, 163, 164]. These paints are used on stone and wood surfaces of buildings, and can also be used for painting of metal over primer, railroad and trolley cars; the coatings produced have high mechanical strength, resistance to wet erosion, and good adhesion to both smooth and porous surfaces.

Recently, a new type of latex based on copolymers of acrylic esters with vinyl acetate has become widely used [80, 131, 165]. The combination of the vinyl acetate links with the acrylic acid ester links in the film former macromolecule allows such important properties to be produced as strength and high elasticity, shine and transparency, good adhesion and water resistance [166].

Detailed study of the physical, mechanical and film-forming properties of latex copolymers of vinyl acetate with various alkyl acrylates such as methyl acrylate, ethyl acrylate, butyl acrylate and 2-ethyl hexyl acrylate have shown that all of these copolymers have good stability, good film-forming properties, and form highly elastic, shiny coats [167]. When small quantities of methacrylic acid are added in the process of copolymerization, the stability of the latexes is significantly increased, their film-forming properties are improved, and the water resistance and adhesion of the coatings formed are increased [168, 169]. The basic area of application of co-polymer vinyl acetate-alkyl acrylate latexes is the manufacture of construction paints; these binders are distinguished by high pigment stability, and the coatings formed, in addition to their high atmospheric resistance, can be produced in a wide variety of colors.

Paint and varnish materials based on other thermoplastic film formers. The latex film formers used in practice include: bivinyl-pyridine latexes, used for soaking and coating in the rubber industry [170]; piperidine-styrene latexes, which form coatings which are highly resistant to the effects of washing agents and have good covering properties [100]; latexes based on a copolymer of bivinyl, styrene and acrylate, forming coatings resistant to mechanical wear and the effects of water [171]; polypropylene latexes, used as a binder for painting of non-fabric materials [172]; copolymers of chloroprene with other monomers [108, 173-176], producing products with a

high degree of dispersion and good elasticity over a broad temperature range, allowing them to be used in the leather industry; copolymers of vinyl chloride and vinylidene chloride [125], frequently used for the production of shiny, heat resistant sound absorbing coatings [175], as well as for the finishing of textile and packaging materials, paper and cardboard [100, 176-178].

Thermosetting Paint and Varnish Materials Based on Latex Film Formers

The problem of the production of latex paint and varnish materials based on thermosetting film formers has been little discussed in the scientific and patent literature [179-183]. The available particles [115, 148-188] on the production of thermosetting latex materials and their hardening discuss primarily carboxylate latexes, which are used in the production of rubber, paper, nonfabric materials and leather. However, works [189-194], published before 1953, do not discuss carboxylic polymer groups as functional groups, i. e., do not note the possibility of hardening of polymers with these groups. Then, Braun began a systematic study of carboxyl-containing polymers [194], [195]. In the USSR, this work was developed by Dolgoploskiy [196 - 199].

Some researchers [200-202], although they produced copolymers with functional groups by latex polymerization, used artificial coagulation, followed by dissolution in an organic solvent; consequently, in actuality they were curing a polymer which was not produced from latex, but rather from the solution. This method was used for hardening of acrylic polymers and their copolymers with acrylonitrile, β-cyanoethyl acrylate, and methoxyethyl acrylate.

The most frequently used chemicals for curing of latex polymers containing carboxyl groups are oxides, oxide hydrates and the salts of polyvalent metals such as zinc, magnesium, calcium and aluminum [203-208].

When the carboxyl group of a polymer interacts with metal oxides, both basic (I) and neutral (II) salts may be produced:

$$-C{\overset{O}{\underset{O-MeOH}{<}}} \qquad \left(-C{\overset{O}{\underset{O-}{<}}}\right)_2 Me.$$

I   II

First, the basic salts is produced, followed (with an excess of carboxyl groups) by the neutral salt, which is partially soluble in the polymer, particularly at the curing temperature (140°C). When the temperature drops, the salts which have been dissolved may precipitate, forming a crystalline sediment. Thus, the bond between the individual polymer molecules is produced on the surface of macroparticles of the metal oxide or due to the crystalline precipitate of basic or neutral salt which settles from the solution. In both cases, the strength of the intermolecular bonds produced is comperable to the crystallization forces in the corresponding basic and neutral organic acid salts. This explains the high tensile strength of latex

polymers cross linked by carboxyl groups. Latexes of carboxyl-containing polymers can be hardened with organic compounds forming covalent bonds. However, the mechanical properties of the free film produced in this manner are lower than when the films are hardened with salts and oxides of metals, as can be seen from the data presented in Table 6.1.

Table 6.1. Mechanical Properties of Films[1] Based on Copolymer[2] Containing Carboxyl Groups Depending on Type of Hardener Used

Hardener	Tensile Strength, kg/cm^2	Rupture Elonga- tion, %	Modulus of Elasticity at 500% E- longation, kg/cm^2
Zinc Oxide	290	590	141
Hexamethylene Diamine Carbonate	196	670	100
Diethylene Triamine	168	525	112
Epoxy Resin (Water-soluble)	114	880	14.6
Urea-formaldehyde Resin (water- Soluble)	98	780	21.2

[1] Drying mode of film: 139°C, 15, min.
[2] Composition of polymer (wt. %); styrene - 50, bivinyl - 47.0, acrylic or methacrylic acid - 3.

The use of organic compounds and metal salts are oxides simultaneously as a hardener allows the production of reticular structure polymers in which there are both covalent and ionic bonds. With proper selection of the resin, rapid relaxation of internal stresses occurs in the coatings formed, the tensile strength is increased, as well as the resistance to instantaneous and impact loads and the heat resistance rises in comparison with coatings with only one type of bond.

Comparatively recently [209, 210], a new hardener was developed -- hexacis methoxyethyl melamine (HMM) [211]
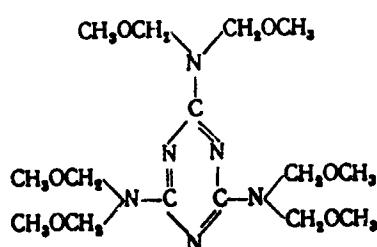
The solubility of HMM in water allows it to be used as a hardener for latex and water-soluble paint and varnish materials.

The low tendency of HMM toward autocondensation allows coatings to be produced with high impact strength. The good compatibility of HMM with a number of other resins greatly expands the assortment of thermosetting coatings.

When HMM is used as a cross-linking agent for polymers containing functional groups, it is used in a ratio of 1 mol to 1.5 mol functional monomer [212, 213]. Carboxyl-containing copolymers can be hardened by HMM at 150°C even without a catalyst, although when 1% p-toluene solfoacid is added, the reaction rate is greatly increased.

Hydroxyl containing copolymers react with HMM only in the presence of a strong acid catalyst, such at p-toluene sulfoacids or phthalic anhydride. The rate of interaction of hydroxyl and amide groups with HMM in the presence of a catalyst is significantly greater than the rate of interaction of carboxyl groups with HMM.

The reaction of HMM with carboxyl-containing acrylic copolymers occurs by replacement of the methoxyl group by a carboxyl group. The reaction between hydroxyl containing copolymers and HMM is essentially a reaction of reesterification.

The properties of the coating produced are also influenced by the pH of the medium in which hardening occurs. Thus, when studies were made [115, 187] of the hardening of films produced from bivinyl styrene latex, containing carboxyl groups, by glycols, it was established that the strength of the films increases and swelling in organic solvents decreases with increasing pH of the medium.

Paint and varnish materials based on thermosetting acrylic copolymers. Ever greater attention is being given to the production of materials of this type [214-218]. This can be explained by the fact that coatings based on acrylic copolymers have valuable properties [219-229].

A number of patents [230-235] contain descriptions of the properties of coatings produced of latex acrylic copolymers, containing various functional groups. Thus, patents [230, 233] suggest self-curing compositions consisting of copolymers of 75-98% alkyl acrylate, 0-5% unsaturated acid nitrile, 0.5-10% monomer with hydrophillic group. Drying of the coating is performed at 140-150°C for 3-30 minutes. The drying process can be accelerated by adding acid catalysts (HCl, H_2SO_4, H_3PO_4). The formation of a reticular coating may occur as a result of self-curing or when such hardeners as HMM, aldehydes, urea or resins containing functional groups are added to the composition of the paint. The properties of coatings based on acrylic copolymers depends on a number of factors: type and number of functional groups in the copolymer, type and quantity of hardener, as well as the presence of absence of pigment.

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The presence of various functional groups in the copolymer has a significant influence on the properties of coatings, as can be seen from the data presented in Table 6.2 for coatings based on styrene-acrylate copolymer latexes with modifying comonomers containing various functional groups [236].

Table 6.2. Properties of Styrene-Acrylate Coatings as Functions of Chemical Nature of Modifying Comonomer[1].

Modifying Comonomer	Quantity of Comonomer, wt. %	Hardness (after Svard)	Impact Strength, kg·cm	Life of Coating in Various Media		
				50% CH$_3$ COOH	5% NaOH	H$_2$O
Acrylic acid	5.0	58	25	0.50	40	720
Acrylic acid Hydroxylethylmethacrylate	1.0 6.8	54	50	0.33	48	120
Acrylic acid Hydroxylethylmethacrylate	1.0 7.4	56	50	0.17	48	720
Acrylic acid Methylolacrylamide	1.0 5.8	60	0	0.08	72	2.4
Acrylic Acid Acrylonitrile	1.0 3.9	58	0	0.17	60	96
Methylolacrylamide	6.6	46	15	0.05	48	2.7

_____

[1] Coatings hardened by HMM.

We can see from the Table presented that the best properties are shown by coatings based on a copolymer containing hydroxyl and carboxyl groups simultaneously. However, in order to produce coatings with the optimal properties, the proper relationship of functional groups must be selected. For example, changing the ratio of acrylic acid to hydroxylmethacrylate in a styrene-acrylate copolymer influences the properties of the coatings formed by hardening with HMM, as can be seen from the data presented below:

Quantity of Comonomer in Copolymer, %	1.0	1.0	1.0
Acrylic acid	3.4	6.8	13.6
Hydroxylmethacrylate			
Properties of coatings			
Hardness (after Svard)	58	54	58
Impact Strength, kg·cm	15	50	50
Life in Various Media, Hr			
50% CH_3COOH	0.25	0.33	0.33
5% NaOH	24	48	48
H_2O	96	120	120

When latex acrylic polymers with functional groups are hardened, the hardener is dissolved or dispersed in water. In both cases, the process occurs in a heterogeneous system, which makes it significantly different from the process of hardening of varnish film formers.

A study of the pecularities of hardening in a heterogeneous system in comparison with a homogeneous system was performed using a copolymer of ethylacrylate and acrylic acid, hardened with HMM in the presence of p-toluene sulfoacids [237, 238]. The polymer was produced by latex copolymerization, which was dissolved for the study of hardening in a homogeneous medium. The study of the kinetics of the hardening process performed using infrared spectroscopy, showed that the hardening reaction rate is higher in the heterogeneous system. The authors give the following explanation for this fact: the carboxyl groups in the latexes based on acrylic acid copolymers are concentrated in the surface layer of the particles [239, 240], and the HMM is concentrated in the space between particles during the process of film formation; as they interact, a gel is formed. Thus, the concentration of functional groups in the reaction zone in a heterogeneous system will be greater than in a homogeneous system, which is the reason for the higher reaction rate in the heterogeneous system. In connection with the great role of the surface in the process of cross-linking of this polymer, the change in the surface of the latex system, defined by the particle size, should influence the degree of cross-linking. A study of this problem [241-243] on the example of latex copolymers of ethylacrylate with methylmethacrylamide, showed that during thermal hardening of latex copolymers containing hydrophillic methylolamide groups by DEG-1[1] resin, the optimal properties of hardened films are achieved with a definite content of methylolamide groups, as can be seen from the data presented below:

Quantity of methylolamide groups in copolymer, mol %	2.55	6.55	8.75	11.43
Maximum water absorption of coatings, %	11.7	4.1	5.0	12.0
Content of gel fraction in dimethyl formamide, %	70	90	91	93
Swelling of gel fraction in dimethyl formamide, %	1500	620	480	407
Equilibrium degree of swelling in dimethyl formamide [244, 245]	18.8	7.4	5.9	5.0

---

[1] The characteristics of DEG-1 resin are: molecular weight 250-300, epoxy group content 21-23%, hydroxyl group content 6-8%, viscosity 45 cp (at 25°C).

When latex copolymers of ethyl acrylate with glycidyl methacrylate are hardened by a water-soluble phenoyl-formaldehyde resin (TU 2309-51), a continuous change in properties of coatings is observed with increasing content of hydrophobic epoxy groups, as we can see from the following data:

Quantity of epoxy groups in copolymer, mol. %	2.55	6.55	11.43
Limiting water absorption of coating, %	100	58.8	24.5
Content of gel fraction in dioxane, %	8.6	89.6	95.0
Swelling of gel fraction in dioxane, %	1050	680	290
Equilibrium degree of swelling in dioxane	13.2	7.9	3.7

The reaction of interaction of epoxy groups with methylo lamide can be judged on the basis of IR-spectral data (Figs. 6.1 and 6.2). The relative change in intensity of absorption bands in the 1020-1080, 1500-1530 and 3200-3400 cm^{-1} bands (see Fig. 6.1) shows that the interaction of the epoxy resin with the methoylamide groups occus most fully with a content of methoylamide groups in the latex copolymer of 6.55 mol. %. When the content of these groups is increased to 11.43 mol. %, a portion of the functional groups failed to take part in the hardening reaction and the hydrophilicity of the unreacted methylol groups facilitates swelling of the film in water. During hardening of a copolymer of ethylacrylate with glycidyl methacrylate by a phenol-formaldehyde resin, the reaction occurs completely with a concent of epoxy groups of 11.43 mol. %, which can be seen from the change in intensity of absorption bands in the area of 912 cm^{-1} (see Fig. 6.2).
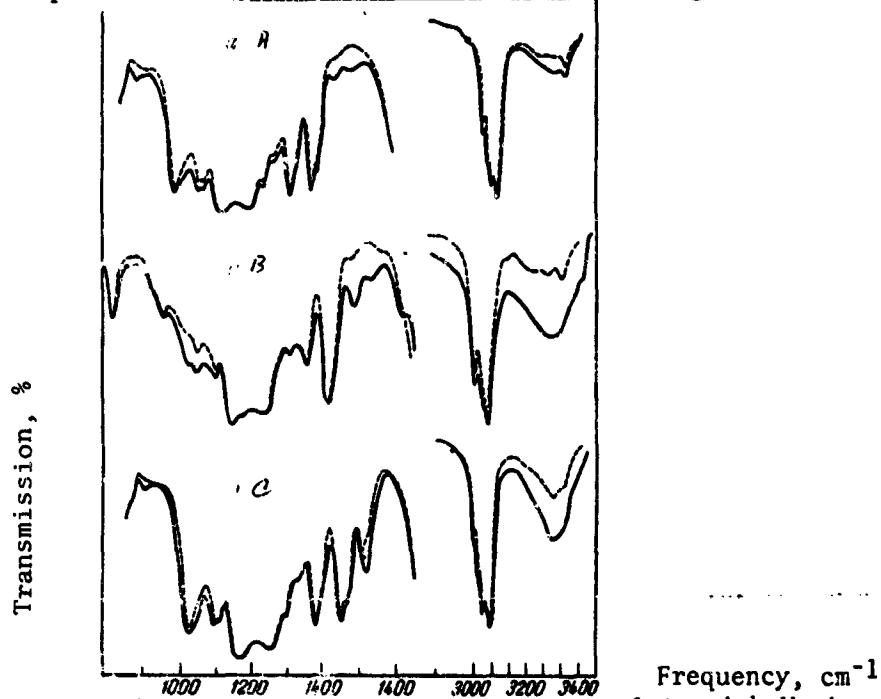
Fig. 6.1. IR-spectra of Films of Copolymer of Ethyl Acrylate with Various Quantities of Methylolmethacrylate (mol. %): a, 2.50; b, 6.50; c. 11.43; ——— initial films; --- films hardened with epoxy resin type DEG-1 at 170°C.
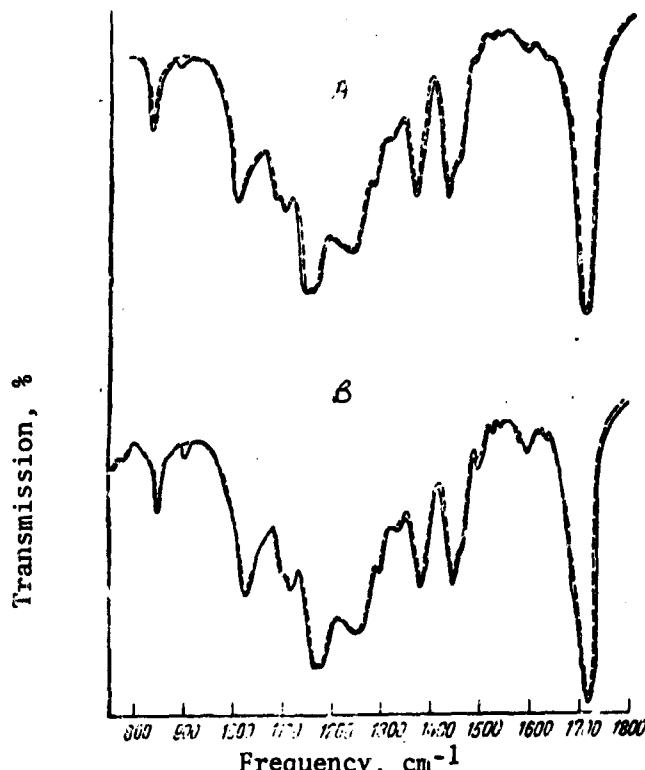
Fig. 6.2. IR-spectra of Films of Copolymer of Ethylacrylate with various Quantities of Glycidyl Methacrylate (mol. %). a; 6.50; b. 11.43; _____ initial films; --- films hardened with phenol formaldehyde resin at 180°C.

The authors explain the results produced by concentration of hydro-phillic methylolamide groups on the surface of the latex particles during the process of copolymerization [246, 247]. As a result, reaction between the hardener, dissolved in water, and the functional groups of the latex copolymer is facilitated. Therefore, there should exist an optimal content of hydrophillic functional groups, resulting from the possibility of their location on the surface of the latex particles and depending, therefore, on the quantity of surface. The groups located on the surface react first of all with the hardener, which, in the process of formation of the coating from the latex, is concentrated in the space between particles. The 3-dimensional reticular structure formed prevents diffusion of hardener into the latex particles, as a result of which the functional groups-located in the volume of the particles remain unreacted. During copolymerization of hydrophobic monomers in aqueous phase, in the case of latex copolymers containing glycidyl methacrylate, the functional groups are located evenly throughout the entire mass of the polymer globule, and the hardening reaction occurs as the hardener diffuses into the globule; there is now optimal content of functional groups as far as the degree of hardening of latex is concerned.

It is possible to produce thermosetting coatings when the polymer subjected to hardening and the hardener are both in the dispersed state. For example, the production of a thermosetting coating has been described [231] with the following composition: latex of acrylic copolymer of 1-10

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mol. % acid with the general formula $CH_2=C(COOH)-(CH_2)_nH$ (where n=1,2) with 90-99 mol. % ester of this acid and an olefatic polyepoxy (water-dispersable) with molecular weight 250-1000. The interaction of the two components produces a coating with good physical-mechanical and usage properties.

The uses of thermosetting acrylic painted varnish material vary. In the motor vehicle industry and other branches of industry, primers based on acrylic latex polymers [248-255] are widely used, sometimes following hot drying. The composition of this sort of primer consists of latexes-copolymers of the acrylic series and plasticizers capable of polymerization, containing 2 double bonds, for example, a latex methylmethacrylate-butylacrylate-diallyl thallate copolymer. This mixture, following application to a degreased steel surface and hardening for sometime at high temperature, produces a high quality, atmosphere resistant coating.

To produce 3-dimensional, chemically stable polymers, acrylic latexes are also combined with epoxy and melamine-formaldehyde resins [256]. The high durability, light and color stability, as well as resistance to dirt and the action of washing agents allow thermosetting acrylic resins to be broadly used as coatings for metals.

Relatively recently, thermosetting acrylate latexes have been synthesized, containing carboxyl, nitrile and amide groups. The presence of these groups helps to cross link the polymer by the formation of hydrogen bonds. No harderner need be used. The coatings produced have a number of properties required for finishing of flexible surfaces: thermoplasticity, good auto-hesion (capability for self-coagulation), low internal stresses and easy internal stress relaxation. All of this has resulted in the wide use of these copolymers in the finishing of leather [257].

Paint and varnish materials based on other types of latex thermosetting polymers. Latex thermosetting materials used in recent times also include: vinyl acetate latexes [259-261], capable of being hardened by phenol and epoxy resins and isocynates; materials based on dienes [262, 263]; vinyla-diene chloride polymers [264-268]. They have good adhesion to fibers such as wood fiber [269-273]. A material has been developed on the basis of a bivinyl-nitrile latex for protection of rolled metal products [258]. Coat-ings with satisfactory physical, mechanical and protective properties are produced [269] by adding a water-soluble alkenyl-phenol resin type VRS (TU P-428-65), to bivinyl-nitrile latex (types SKN-26-IKh and SKN-40-IKh).

The Dow Chemical Corp. produces a latex in the bivinyl-styrene polymer group for protection of metals [250]. Coatings based on this latex have high adhesion to the metal surface, and are resistant to the effects of water and mineral oils. The Reichhold Chem. Corp. has developed a material based on alkyd resins which forms and elastic coating with good shine following hot drying (at 138°C for 30 minutes). However, insufficient experience has been accumulated in the use of thermosetting latex materials for the protection of metals. They are now used as primers, since coatings based on them do not have sufficient strength and decorative properties.

Materials Based on Varnish Film Formers

Varnish film formers are historically the first synthetic polymerization film formers used in the paint and varnish industry. In spite of their significant shortcomings (toxicity and fire danger of solvents, low content of dry matter at useable viscosity, etc.), they are still widely used in the paint and varnish industry. This is explained by the simplicity of their manufacture and the absence of components such as emulsifiers, regulators, etc., which worsen the anti-corrosion and dielectric properties of coatings.

At the present time, the paint and varnish industry uses primarily polymerization film formers based on chlorine-containing vinylic resins and their copolymers. Resins based on acrylic and methacrylic acid esters are less expensively used, although each year the volume of production of acrylate film formers and coatings based on them is increased. Paint and varnish materials based on polyvinyl acetals, cumarone-indene resins, etc. are also used.

Thermoplastic Paint and Varnish Materials Based on Varnish Film Formers

Pain and varnish materials based on chlorene containing vinyl resins are widely used in industry as primers, fillers and enamels. They are used as a basis for coatings with good protective properties, high strength, atmospheric resistance, low permeability, resistance to the influence of acids, alkalis and various oils, as well as open flame. However, polymers based on chlorene containing monomers alone have many significant short-comings: poor compatibility with plasticizers and most resins, formation of highly viscous solutions in organic solvents, presenting the production of varnish with high contents of dry matter and forcing the use of expensive active solvents. The coatings have weak adhesion and low decorative properties. These shortcomings can be eliminated by combined polymerization of vinyl chloride with other monomers -- vinyl acetate, vinyl alkyl esters, acrylic and methacrylic acid esters, etc. -- or additional chlorination of the poly-vinyl chloride.

The greatest interest is in paint and varnish materials based on co-polymers of vinyl chloride with vinyl acetate. They combine resistance to atmospheric influences, oils and chemical reagents with good mechanical and dielectric properties and high elasticity. The copolymer is frequently saponified to increase its compatibility with other resins; this forms hydroxyl groups and allows production of coatings with reticular structure with good adhesion to the substrate.

In the USSR, copolymer A-15(BTUP-13-55) is produced, containing 85% vinyl chloride and 15% vinyl acetate, as well as type A-15-0(BTUP-14-55) -- a partially saponified copolymer of the same initial composition. Similar copolymers are produced by the American Union Carbide Company under the trade names VYHH and VYGH.

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Vinyl chloride copolymers with vinyl acetate are dissolved in dioxane, chlorinated hydrocarbons, complex esters, ketones, and are insoluble in alcohols and parafin hydrocarbons. Film formers based on vinyl chloride copolymers with vinyl acetate are used in the manufacture of phosphate-tizing [274] and protector [275] primers, as well as enamels for painting of agricultural machinery, machine tools, underwater structures and ships [276].

Type A- 5-0 copolymer is used as a basis for the production of oil-resistant nonfouling enamels [277].

There is interest in copolymer VKhVD-40 (VTUMKhP 3540-52), consisting of 60% vinyl chloride and 40% vinylidene chloride. Films of this copolymer are elastic and rather strong [278]: the relative elongation reaches 300%, the tensile strength is 1-1.5 kg/cm^2. Coatings based on this copolymer have high chemical resistance, are nonflammable, but due to their low light resistance, they are used primarily for interior painting. A similar co-polymer is produced in the USA under the trade name Geon 200×20.

Coatings based on copolymers of vinyl chloride with vinyl alkyl esters, have the hardness of vinyl chloride polymers plus somewhat greater adhesion and elasticity. Type SKhB-70 copolymer has been developed, containing 70% vinyl chloride and 30% vinyl butyl ester, as well as type SKhBM-20, consisting of 70% vinyl chloride, 20% vinyl butyl ester and 10% methylacrylate. The presence of the methyl acrylate in the resin increases its solubility and improves adhesion and elasticity of its coatings. Copolymers SKh-70 and SKhM-10 dissolve in Xylene, toluene, butyl and ethyl acetate, are com-patible with alkid, phenol-formaldehyde and other resins. These copolymers are used to produce paint and varnish materials which form atmosphere and water-resistant coatings, and are therefore recommended for painting of bridges, ships, etc. [279]. Coatings based on these copolymers have greater atmosphere resistance than oil-base coatings, and superior adhesion to chlorinated polyvinyl chloride coatings [280].

As we have noted, the poor solubility of polyvinyl chloride can be eliminated by additional chlorination. Usually, chlorination is performed until the chlorine content reaches approximately 64%, corresponding to the introduction of 1 chlorine atom for each three polyvinyl chloride macro-molecule links. Further chlorination sharply worsens the solubility of the chlorinated vinyl chloride resin. In the Soviet Union, two types of chlorinated polyvinyl chloride resin are currently produced: type PSKh-S (medium viscosity) and type PSKh-N (low viscosity) [281]. These resins, in comparison with polyvinyl chloride resins, are more stable during storage and dissolve in less active solvents; coatings based on these resins have somewhat greater adhesion, but lower light and atmosphere resistance. Chlorin-ated polyvinyl chloride coatings are resistant to the effects of water, oils, acids, alkalis and corrosive gases, but are not very heat resistant.

Paint and varnish materials based on chlorinated polyvinyl chloride resins are widely used for painting of various objects used under moderate and tropical climate conditions in contact with water and various corrosive media. These objects include: equipment and apparatus used in chemical, petroleum, road building and agricultural machine building, machines and metal structures exposed to river water and sea water [282], the exteriors of commercial, public and residential buildings [283].

Paint and varnish materials based on acrylic and methacrylic acid esters (acrylate film formers) began to be used for the production of protective coatings in the 1930's. At the present time, they occupy a leading position among all polymerization film formers. This rapid growth of the production and consumption of acrylate film formers can be explained by the development of a continuous method for the production of the initial acrylic monomers, as well as the remarkable properties of coatings based on them.

Acrylate film formers are transparent and colorless and do not interact with pigments; therefore, enamels based on them have high stability in storage. Coatings based on them are distinguished by their good decorative properties, high adhesion to various surfaces, good resistance to the effects of acids, alkalis, oils, water and washing agents, good electrical insulating properties; furthermore, they do not change color when subjected to ultra-violet radiation and high temperatures.

The properties of acrylate film formers depend to a great extent on the alkyl radical of the ester group in the side chain of the polymer. For example, films of polymethyl acrylate are rigid, have moderate hardness and their relative elongation amounts to around 750%. Films of polyethyl acrylate of the same molecular weight are considerably softer and more elastic than films made of polymethyl acrylate. The relative elongation of films of polyethyl acrylate is around 1800%. The corresponding low polymer esters of methacrylic acid are significantly more rigid and harder than polyacrylates, which is explained by the presence of the methyl group at the α-carbon atom.

Acrylic and methacrylic monomers copolymerize well with each other and with other monomers, for example, with styrene, vinyl acetate, acrylonitrile, etc. This allows production of copolymers forming coatings with various physical and mechanical properties. When acrylate film formers are used, there is no need for special plasticizers, which migrate out of the coating with the passage of time, worsening its usage properties. Both nonpigmented and pigmented paint and varnish materials are produced on the basis of these film formers.

Dissolution of acrylic polymers requires rather active solvents. For example, some copolymers are soluble in esters, toluene, Xylene or various chlorinated hydrocarbons, while other acrylic polymers are soluble only in ketones such as methylethyl ketone.

In the Soviet Union, acrylic resins [284] types BMK-5 (TU MKhP 2473-51) and AS (TU 74-56) are produced for the manufacture of paint and varnish material. They are compatible with pigments and various resins, for example, mellamine-formaldehyde, chlorinated polyvinyl chloride, low-viscosity epoxy, nitrocellulose and alkyd resins. Their good adhesion to metals allows acrylic

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resins to be used for the manufacture of primers for tropical conditions. Type AS-72 enamel (TU MKhP 241-60), pigmented with rutile titanium dioxide, is manufactured on the basis of resin PMK-5, melamine-formaldehyde resin and ethyl cellulose.

The comparatively high vapor permeability of films based on acrylic varnish film formers in comparison, for example, to films made of chlorinated polyvinyl chloride resin, limits the possibility of utilization of these films for the protection of metals with low conversion resistance, but they are successfully used for the protection of aluminum and its alloys. Most aluminum window frames produced in the USA are coated with air-dried methacrylate varnish [285]. This varnish is completely transparent and presents discoloration of aluminum frames, which come in contact with lime solutions during the process of construction. The varnish also protects the metal well from the effects of acids, used in the etching of concrete surfaces. Due to their neutrality to pigments, acrylate film formers are used as the base of fluorescent and phosphorecence coatings for aircraft and motor vehicles.

Acrylate varnishes are used for finishing of products of brass and copper which darken when exposed to sulfur fumes [286].

Paint and varnish materials based on acetals of polyvinyl alcohol are quite broadly used in the paint and varnish industry. Polyvinyl acetols (polyvinyl formal, polyvinylethylal, polyvinylbutyral, etc.) are produced from polyvinyl acetate or polyvinylalcohol by the action of the corresponding aldehyde in the presence of an inorganic acid (sulfuric or hydrochloric), causing hydrolis of the polyvinyl acetate and catalytic acetalation of the polyvinyl alcohol. Solvents used for polyvinyl acetols include alcohols, cresols, mixtures of complex esters, ketones, simple glycolic esters and chlorine-containing solvents.

Polyvinyl acetal coatings have good adhesion, resistance to the effects of water, oils and gasoline.

Polyvinyl butyryl is most frequently used as a film former. Polyvinyl butyryl resins are quite compatible with glyphthalic and phenol-formaldehyde resins, soluble in alcohols, with urea-or mellamine-formaldehyde resins.

Alcohol varnishes based on polyvinyl butyryl, modified with mellamine, formaldehyde resins, are used for the protection of metals, in particularly, cans [287]. These coatings have good impact strength.

Polyvinyl acetols are widely used as electrical insulation coatings [288]. Phosphatizing primers are produced on the basis of polyvinyl butyryl [289].

Thermosetting Paint and Varnish Materials Based on Varnish Film Formers

Paint and varnish materials based on acrylic resins containing carboxyl groups. Carboxyl-containing resins are produced by introducing 3-25% mono- or dibasic unsaturated acids or their anhydrides to the copolymer composition.

Usually, acrylic and methacrylic acids and maleic anhydride are used, due to their availability and comparatively low cost. It is also recommended that fumeric, itaconic and aconitic acids be used [8, 290].

The commonest copolymer is one containing 72% styrene or vinyl toluene, 20% ethylacrylate and 8% methacrylic acid. Paint and varnish materials based on this copolymer, hardened with epoxy resins, such as Epon 828 produced by the Shell Chemical Company, have good decorative and protective properties.

Carboxyl-containing acrylic resins are hardened with various epoxy resins [10, 21, 291-306], mellamine and urea resins [24, 307-309], glycols, diisocynates, salts of polyvalent metals [23], or by cross linking [15]. Hardening of epoxy resins is performed at 160-185°C for 25-30 minutes. The hardening time and temperature can be reduced by introduction of catalysts such as tertiary amines [297] or quarternary ammonium bases [292, 310, 311]: trimethyl docecyl ammonium chloride, trimethyl amino ethyl phenol, a complex of piperidiene with boron trifluoride, etc. The hardening reaction can be accelerated by introducing small quantities of vinyl pyradiene [312, 313], or some other unsaturated amine as an internal catalyst. Brockman [314], in contrast to the data presented above, states that carboxyl-containing resins can be stabilized with long-chain tertiary amines.

Coatings based on thermosetting acrylic resins hardened with epoxy resins have good adhesion, chemical resistance, in particular resistance to washing agents, alkalis and acids, and high light resistance. The hardening of carboxyl containing copolymers with glycols occurs according to the following reaction:

$$2 \cdots -\overset{\text{O}}{\overset{\|}{C}}-OH + HOCH_2RCH_2OH \longrightarrow$$
$$\longrightarrow \cdots -\overset{\text{O}}{\overset{\|}{C}}-O-CH_2-R-CH_2-O--\overset{\text{O}}{\overset{\|}{C}}- \cdots + 2H_2O$$
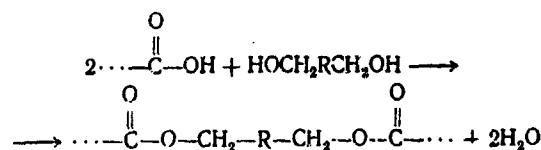
A similar reaction occurs upon hardening of mellamine-and urea-formaldehyde resins at 150°C for 30 minutes. In order to avoid autocondensation of the nitrogen-containing resins, they are preliminarily treated with butanol [306, 307], converting the alkoxyl groups to butoxyl groups.

Hardening by salts of polyvalent metals can be performed at room temperature, but this produces a low quality coating, primarily due to the low water resistance.

Paint and varnish materials based on acrylic resins containing hydroxyl groups are not as common as materials based on carboxyl-containing resins. This is explained by the difficulty of producing hydroxyl containing resins. They can be produced by copolymerization with monoacrylates, glycols, oxyethyl- or oxypropyl methacrylates [10, 294, 315-318], or indirectly from other available monomers. Kelly, Melrose and Solomon [2] produced a hydroxyl-containing copolymer by boiling an epoxy-containing copolymer with diethylamine:

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$$\cdots-CH_2-\underset{\underset{\underset{\underset{\underset{\underset{O}{\overset{|}{CH_2-CH-CH_2}}}{\overset{|}{O}}}{\overset{|}{O=C}}}{\overset{|}{C}}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\underset{\bigcirc}{CH}-\cdots + (C_2H_5)_2NH \longrightarrow$$

$$\longrightarrow \cdots-CH_2-\underset{\underset{\underset{\underset{\underset{N(C_2H_5)_2}{\overset{|}{CH_2-CH-CH_2OH}}}{\overset{|}{O}}}{\overset{|}{O=C}}}{\overset{|}{C}}}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\underset{\bigcirc}{CH}-\cdots$$
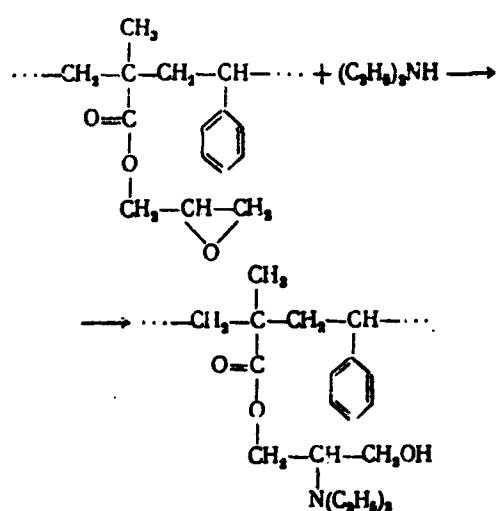
Hydroxyl groups can be introduced into the copolymer also by the interaction of carboxyl containing copolymers with compounds containing epoxy groups in the presence of bases [319, 320]:

$$\cdots-CH_2-\underset{\underset{COOH}{|}}{CH}-CH_2-\underset{\underset{COOR}{|}}{CH}-\cdots + CH_3-CH_2-\underset{\diagdown\ \ \diagup}{\underset{O}{CH-CH_2}} \xrightarrow{(C_2H_5)_3N}$$

$$\cdots-CH_2-\underset{\underset{\underset{\underset{CH_3-CH_2-CH-CH_2OH}{\overset{|}{O}}}{\overset{|}{C=O}}}{|}}{CH}-CH_2-\underset{\underset{COOR}{|}}{CH}-\cdots$$

$$\longrightarrow$$
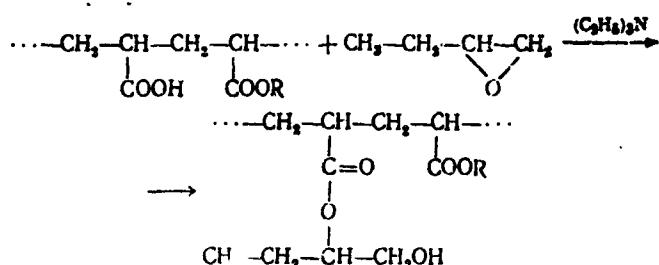
The hydroxyl containing resins are hardened by various amino resins in the presence of an acid catalyst, for example, p-toluene sulfo acids, or without it [306, 321-323]. These systems are compatible and stable upon storage. They are hardened at 125-130°C in 30 minutes by the reaction

$$\cdots-R-\underset{\underset{O}{\|}}{C}-O-CH_2-\underset{\underset{OH}{|}}{CH_2} + \cdots-\underset{\underset{}{C}}{C}\underset{}{}C-\cdots \longrightarrow$$

(with structure: R'—O—CH₂—NH attached to triazine ring)

$$\longrightarrow \cdots-R-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_2\cdots-C\ \ C-\cdots + R'OH$$

(with structure: —O—CH₂—NH attached to triazine ring)

-150-
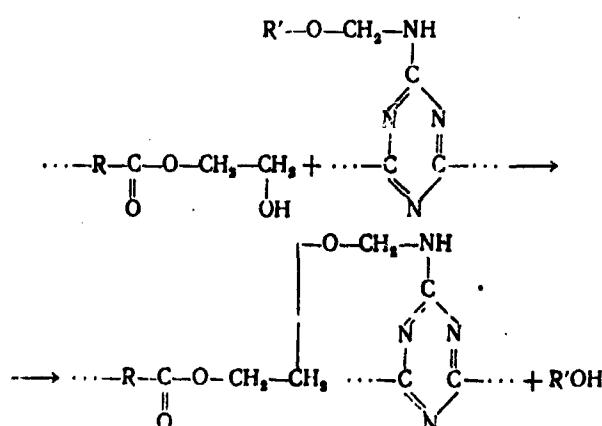
Hydroxyl-containing resins are hardened by diisocynates at room temperature [324-32]. They can also be hardened by diepoxides [328] and phenol resins [321]. Acids are introduced to give the coatings high adhesion to metals and accelerate the hardening reaction. The acid acts as an internal catalyst [329, 330].

To improve the operational properties of the coatings, hydroxyl-containing resins are modified with alkyd resins.

Paint and varnish materials based on acrylic resins containing epoxy groups are less frequently used than the materials described above. The epoxy groups are introduced to the resin by copolymerization with glycidyl acrylate, gylcidyl methacrylate and other unsaturated compounds containing the epoxy ring [331-334]. Resins of this type are hardened by primary amines or polyethylene polyamine [333]. The olefatic amines react with the copolymer epoxy groups at room temperature, forming a polymer coating of reticular structure

$$\cdots -CH_2-CH-CH_2-N-CH_2-CH-CH_2-\cdots$$
$$OH \qquad | \qquad OH$$
$$R$$
$$OH \qquad | \qquad OH$$
$$\cdots -CH_2-CH-CH_2-N-CH_2-CH-CH_2-\cdots$$
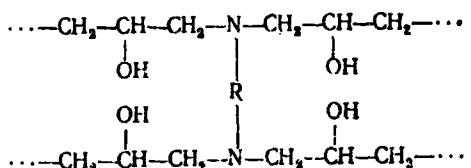
The hardener for acrylic resins containing epoxy groups is polyethylene polyamine. Coatings produced from this composition have very good adhesion. In order to reduce the hardening temperature without increasing hardening time, glycols are usually introduced as catalysts. One shortcoming of polyethylene polyamine is its toxicity.

The aromatic amines hardened resins of this type under more rigid conditions (temperature, hardening time) than olefatic resins [335], but the coatings produced have better protective properties.

Quite frequently, acrylic resins containing reactive epoxy groups are hardened using low-molecular polyamide resins, products of the condensation of polyamines with olefatic dicarboxylic acids. The hardening mechanism of low molecular polyamide resin is quite similar [336] to the mechanism of hardening by polyfunctional amines. The coatings produced have good physical mechanical and protective properties, the properties of the coatings depending on the molecular weight of the polyamide resin and its amine number.

Acrylic copolymers containing epoxy groups are hardened by dibasic carboxylic acids or their anyhydrides [332, 333] in the presence of tertiary amine catalysts, particularly triethyl amine or quarternary ammonium salts according to the reaction

$$2 \cdots -CH_2-CH-CH_2 + R(COOH)_2 \longrightarrow$$
$$\underset{O}{\diagdown\diagup}$$

$$\longrightarrow \cdots -CH_2-CH-CH_2-O-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-O-CH_2-CH-CH_2-\cdots$$
$$\underset{OH}{|} \qquad\qquad\qquad\qquad\qquad\qquad \underset{OH}{|}$$
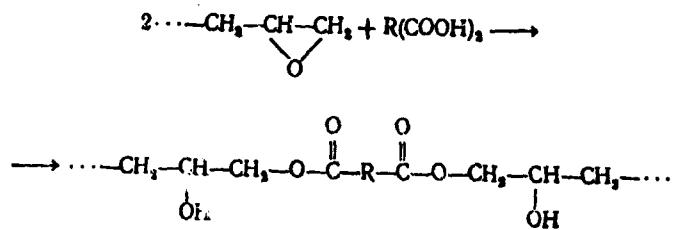
Coatings hardened by acids have better physical and mechanical properties and coatings hardened by amines, but the hardening temperature must be 100-150°C [333].

Hardening by acid anhydrides is conducted in the presence of 0.5% amine catalyst [337, 338] at 170°C for 30 minutes.

Coatings with satisfactory properties are produced by hardening of these acrylic resins with phenol-and amino-formaldehyde resins [332, 339]. The hardening mechanism by these resins it has not been sufficiently studied.

Other hardeners used are mineral acids [333, 340] such as hydrochloric acid and isocyanates [341].

Thermosetting acrylic resins with epoxy groups in the side chain have not yet become widely used industrially, since the initial monomers are expensive, toxic and quite reactive. The high activity of epoxy groups requires careful selection of solvents, pigments and catalysts in order to produce stable, low viscosity resins which wet the pigment well. The problem of stabilization of epoxy-containing resins is an important one, due to the ability of these resins to undergo spontaneous hardening according to the reaction

$$\cdots-CH_2-CH-CH_2 + H_2C-CH-CH_2-\cdots \longrightarrow$$
$$\underset{O}{\diagdown\diagup} \qquad\qquad \underset{O}{\diagdown\diagup}$$

$$\longrightarrow \cdots-CH_2-CH-CH_2$$
$$\underset{O}{|}\quad\underset{O}{|}$$
$$\underset{CH_2-CH-CH_2-\cdots}{|\qquad|}$$
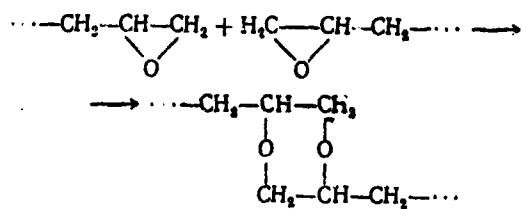
It has been suggested [333, 342], that phosphoric acid and ketones be used as stabilizers. The stabilization mechanism is reduced to the following reaction:

$$\cdots-CH_2-CH-CH_2 + H_3PO_4 \longrightarrow \cdots-CH_2-CH-CH_2$$

$$O=P(OH)_2$$

$$\cdots-CH_2-CH-CH_2 + R-C-R' \longrightarrow \cdots-CH_2-CH-CH_2$$
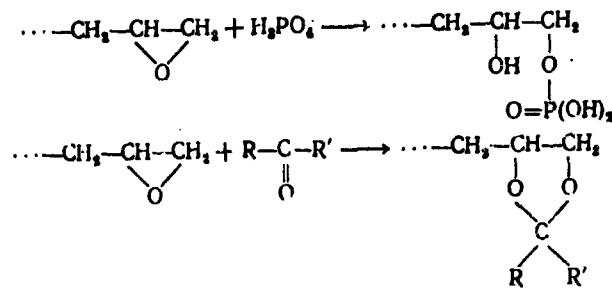
This produces solutions of resins which are stable at room temperature for an unlimited time. Coatings based on these resins have very good anti-corrosion properties, good adhesion, high impact strength, hardness, resistance to the effects of water, solvents, oils and washing agents.

Paint and varnish materials based on acrylic resins containing amide groups are attracting attention from researchers each year. Resins of this type are produced by using acrylomide or methacrylomide as the reactive conomomer [343, 344]. When the resin is treated with formaldehyde, methylol derivatives are produced:

$$\cdots-C-NH_2 + CH_2O \xrightarrow{H^+} \cdots-C-NH-CH_2OH$$
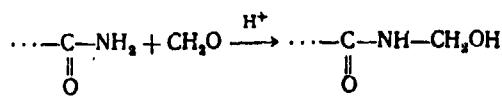
In an acid medium, the methylol groups have a tendency toward gel formation; therefore, in order to increase the stability of the resin, they are esterified, most frequently with butynyl [2, 10-12, 18, 345, 346].

Methylol groups can be introduced to the copolymer directly by copolymerization of methylol acrylamide or methylolmethacrylamide with other monomers, bypassing the condensation stage [345, 347-352].

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Sekmakas and Stenkl [transliterated from Russian -- correct spelling unknown] showed [353] that the copolymers of acrylamide can be produced by a single-stage method using alkyline catalysts. Copolymerization and methylolation are performed simultaneously in the presence of unsaturated polyesters; this produces copolymers with high stability and good film-forming properties.

Amide type polymers can be produced from carboxyl containing copolymers and amino alcohols [354]. Modification of carboxyl containing acrylic copolymers with certain amino alcohols is used to produce thermosetting oxasoline polyacrylates [355]:

$$\cdots -CH_2-CH-\cdots + H_2N-\underset{\underset{R \quad R'}{\diagup}}{C}-CH_2OH \longrightarrow$$
$$\underset{\underset{OH}{|}}{\overset{\overset{\displaystyle C=O}{|}}{}}$$

$$\longrightarrow \cdots -CH_2-CH-\cdots \longrightarrow \cdots -CH_2-CH-\cdots$$
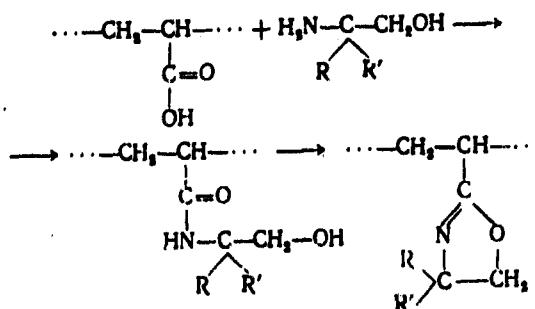
The amino alcohols used in this case are tris-oxymethyl aminomethane, 2-amino-2-methyl-1,3-propanediol, 2-amino-2-methyl propanol.

An oxasolic thermosetting copolymer has been produced from carboxyl containing resin of the following composition: 25-35 wt parts styrene, 40-60 wt parts alkylacrylate and 10 wt parts acrylic acid.

Usually, the amide content in the copolymer does not exceed 30%, since when this quantity is exceeded, brittle films are produced. An improvement in elasticity is achieved by combination with polyesters, but a more effective method is grafting of unsaturated polyester to the polymer chain.

Methylolated amide copolymers can undergo spontaneous cross-linking at 160-170°:

$$2 \cdots -\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-OH \xrightarrow[-H_2O]{}$$

$$\longrightarrow \cdots -\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-O-CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\cdots \xrightarrow[-CH_2O]{}$$

$$\longrightarrow \cdots -\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-NH-\overset{\overset{\displaystyle O}{\|}}{C}-\cdots$$

$$\cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-OH + RO-H_2C-NH-\underset{\underset{O}{\|}}{C}-\cdots \longrightarrow$$

$$\longrightarrow \cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\underset{\underset{O}{\|}}{C}-\cdots + ROH + CH_2O$$

$$2\cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-OR \longrightarrow$$

$$\longrightarrow \cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-NH-\underset{\underset{O}{\|}}{C}-\cdots + R-O-CH_2-O-R$$
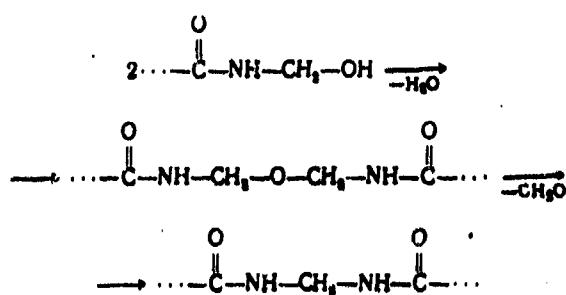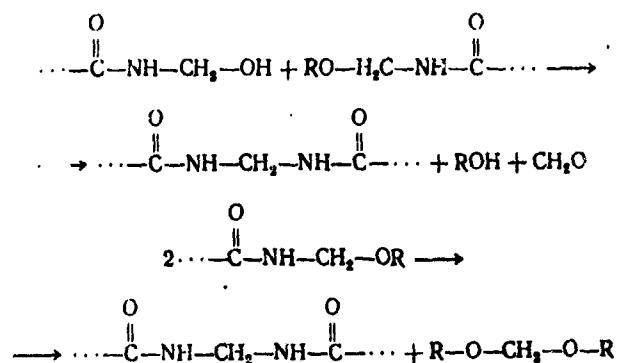
The introduction of acid catalysts such as p-toluene sulfo acids can decrease the hardening temperature to 150°C [356].

Phenol-, urea- and melamine-formaldehyde [352] and epoxy [353] resins can be used to cure amide resins. The curing of amide resins with hydroxyl containing resins occurs according to the following reaction:

$$\cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-OR + HO-R'-\cdots \longrightarrow$$

$$\longrightarrow \cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-O-R'-\cdots + ROH$$
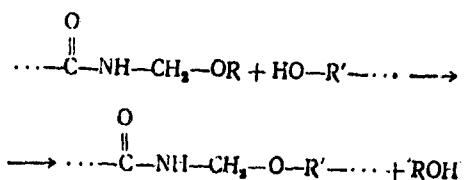
The interaction of the methylol groups of the resin with epoxy resins causes the formation of a 3-dimensional structure polymer:

$$\cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-OH + H_2C-CH-\cdots \longrightarrow$$

$$\longrightarrow \cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-O-CH_2-\underset{\underset{OR}{|}}{CH}-\cdots$$
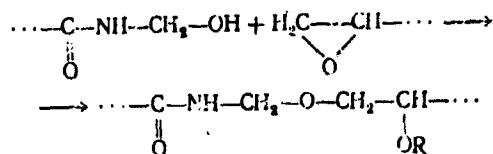
Amide type resins can be cured with isocyanates:

$$\cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-OH + R(NCO)_2 \longrightarrow$$

$$\longrightarrow \cdots -\underset{\underset{O}{\|}}{C}-NH-CH_2-O-\underset{\underset{O}{\|}}{C}-NH-R'-NH-\underset{\underset{O}{\|}}{C}-O-CH_2-NH-\underset{\underset{O}{\|}}{C}-\cdots$$
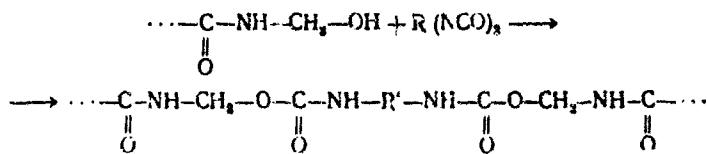
Thermosetting acrylic amide type resins form coatings with good adhesion, resistance to the effects of solvents, washing agents, water, light and the atmosphere.

The production of coatings of copolymers of vinylesters of branched carboxillic acids with acrylomide, treated with formaldehyde in butynol, has been described. The hardeners used are amino formaldehyde or epoxy resins; the hardening temperature is 150°C. Introduction of acrylic acid to the copolymer (up to 5%) results in the formation of a copolymer which cross links spontaneously at 150°C. These coatings have good resistance to the effects of water, alkalis and detergents.

In the Soviet Union, a number of thermosetting acrylic copolymers have been produced, containing reactive metholamide groups [359], [360]. They are designed for the production of varnishes and enamels for various purposes. The copolymers are hardened by melamine or epoxy resins. Coatings based on these copolymers have good adhesion to various metals and primers, high mechanical strength, atmospheric resistance and marvelous decorative properties. Enamels based on these copolymers are used for painting of products used under tropical climate conditions.

Hardeners. Most cross-linking agents used for hardening of thermosetting polymerization resins are either amines or epoxy resins. Amine resins have been known for some time [361], while epoxy resins began to be used only in 1957-1958 [362].

Melamine and urea resins, used as hardeners, are treated with butanol [352] to decrease their tendency toward autocondensation. However, the presence of both butoxyl and methalol groups as well as secondary amino groups, still causes the functional groups within the resin to interact. Since the rates of the reactions of hardening and autocondensation are of the same order of magnitude, the formation of polymerized resin blocks in the cured coating worsens the properties of the coatings.

A new hardener developed recently, hexakis-methoxymethyl melamine [209-211] does not have this shortcoming of amino resins, since at the hardening temperatures used for polymers, the cross-linking reaction occurs many times more rapidly than its autocondensation [329].

Epoxy resins of two types are used as hardeners: aromatic and olefatic. When thermosetting acrylic resins are hardened with epoxy resins, coatings are produced with good adhesion to the substrate, resistant to the effects of solvents.

Coatings based on thermosetting acrylic resins, hardened with olefatic epoxy resins, have better atmospheric resistance and greater elasticity than coatings hardened with aromatic epoxy resins based on diphenyl propane [363]. Resins of olefatic structure have lower viscosity and therefore require the introduction of a small quantity of solvent. In order to avoid destruction under the influence of ultraviolet rays, glycidyl acetate [364], glycidyl sebacinate [365] and epoxidized oils [366] are used as hardeners.

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It is recommended that thiocyanic acid salts be used to accelerate hardening of resins containing carboxyl and hydroxyl groups [367].

The patent literature contains reports of the use of phenol-formaldehyde [368-370] and cresol-formaldehyde [371] resins as hardeners, although they can be used only in primers due to their natural dark color.

It is suggested that urea derivatives be used as hardeners -- acrylylurea, benzoguanaminformaldehyde [372, 373], and dimethylolethyleneurea [318, 374], trimethylolmelamine [375], acrylyldicyanodimide, acrylyltriazine, cyclical alkylene imido phosphonitriles [376], n-dodecyl succinic anhydryde [377], the products of interaction of aldehydes with aromatic diamenes [378].

Self-hardening paint and varnish materials have not as yet been widely used. This is explained by the fact that these materials are insufficiently stable on storage, since the resins are copolymers of two or more reactive monomers, the functional groups of which can interact with each other. Interaction of reactive groups within one macromolecule is also possible, which greatly worsens the properties of the coatings; therefore, certain quantities of hardeners, most frequently amino resins, are always added to the composition. During formation of coatings, the reactions between the functional groups of the different macromolecules are complicated by spatial hinarances, and only a portion of the groups can react.

The literature contains descriptions of paint and varnish materials based on resins containing the follwing reactive groups simultaneously: carboxyl and epoxy [390, 379-384], hydroxyl and epoxy [385], carboxyl and methylol [386, 387], carboxyl and hydroxyl [388], [389], hydroxyl and amide [390], hydroxyl and methylol [391].

Paint and Varnish Materials Based on Water-Soluble Film Formers

The presence of functional groups in materials of this type allows all of them to be considered thermosetting paint and varnish materials.

Paint and varnish materials based on alkali-soluble film formers have the greatest practical significance.

The composition (N %) of alkali-soluble film formers used for the production of paint and varnish materials is presented below:

Recipe Nr.	Acrylic Acid	Methacrylic Acid	Acrylonitrile	Acrylic Acid Amide	Alkyl acrylate	Styrene	Butadiene	Biblio Ref
1	10-.0	-	2.5-25	-	25-50	-	-	392
II	50-8ö	-	2-10	2-30	2-10	-	-	392
III	15-20	-	3-7	10-25	50-70	-	-	393
IV	-	5-20	-	-	80-90	-	-	394
V	25	-	-	-	70	5	-	395
VI	-	40	-	-	-	-	50	396
VII	-	15	-	-	82	3	-	397

Almost all types of hardeners used for varnish thermosetting systems can be used to harden these film formers. The only additional requirement which must be placed on the hardener is its solubility in water.

In the following paragraph, we will analyze the properties of hardeners most frequently used for curing of water-soluble treated varnish materials.

Products of condensation of formaldehyde with amines. The most important representative of this group is the hexa-kis-methoxyethyl melamine (HMM) described earlier [221]. In order to increase the rate of hardening of water-soluble polymers in the presence of HMM, strong acid catalysts can be introduced [398]. However, in most water-soluble polymers, consisting of ammonium salts or amine salts, an acid catalyst is contained within the polymer in latent form. As the salt is decomposed upon heating, the ammonia or amine evaporates, and the regenerated carboxyl groups acts as a catalyst. The hardening of acrylic polymers by HMM is performed [255] generally at a temperature 150°C for 30 minutes. At lower temperatures, the degree of hardening is decreased and, consequently, the strength of the coating produced is reduced. Optimal relationships of hexa-kis-methyoxymethyl mellamine and carboxyl groups have been found: 1 mol HMM per 1.5 mol carboxyl containing monomer.

When tetra-kis-(methyoxmethyl)-benzoguanimine [399] is used as a hardener, materials are produced having greater stability during storage and forming coatings with a good shine. However, this hardener is more hydrophobic and somewhat more expensive than HMM.

Among hardeners of this class, N, N'-bis-(methoxymethyl)-urea is also used, although it is a less effective hardener than HMM.

Products of condensation of formaldehyde with phenols. Of this group of compounds, the most frequently used are uncondensed phenol alcohols or phenol alcohols with a low degree of condensation. In order to produce water-soluble hardeners of this type, efforts are made to prevent the formation of the reticular structure by introducing substituents to the phenol at the ortho and para positions. The substituted phenols interact with formaldehyde in the presence of alkalis at 30-60°C according to the reaction

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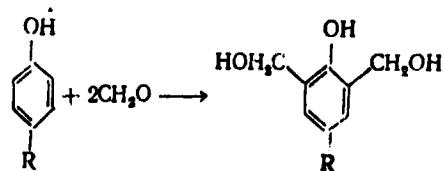
Ef R=CH$_3$-, the produce produced is fully soluble in water. If R=CH$_3$-CH-CH$_2$,

CH$_3$

the solubility of the product produced in water is limited.

Hardening in the presence of phenol-formaldehyde resins must be performed at 170-180°C, which causes yellowing of coatings [400].

Products containing epoxy groups. Epoxy resins, insoluble in water, are frequently used for hardening of carboxyl containing varnish polymers. Recently, epoxy resins with limitless water solubility were synthesized, products of the condensation of epichlorhydrin with olefatic glycols such as mono-, di-and triethylene glycol [401].

However, their use is limited due to the presence of chlorine ions in the hardener, which may cause corrosion of a painted metal surface.

Hardeners of other types. These hardeners are encountered much more rarely. For example, carboxyl containing polymers can be hardened by a zirconium-ammonium complex at room temperature [402], [403]. Hardening is achieved by the interaction of carboxyl groups with the ions of zirconium as follows:
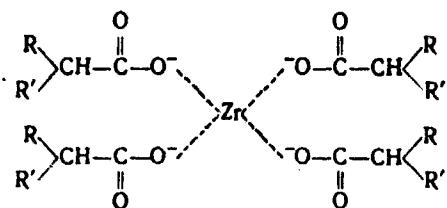
The zirconium is introduced as zirconyl ammonium carbonate (NH$_4$)$_3$HZr (CO$_3$)$_3$ or by the formation of a complex of water-soluble zirconium oxichloride and ammonium oxide hydrate in the presence of the corresponding copolymer [403].

Systems are known which can be hardened by interaction of the polymer with the surface material [404]. For example, water-insoluble coatings can be produced on plaster by the formation of ionic bonds between the carboxyl groups of the film former and the calcium ions contained in the plaster.

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Descriptions have been published of hardening of carboxyl-containing polymers by complex formation with boric acid; by esterification with diacids in the presence of aldehydes [405]; by the formation of chelates with such metals as titanium; by the use of bivalent metal salts, as well as metal oxides [406].

Paint and varnish materials based on self-hardening alkali-soluble film formers. Among the most important self-hardening products based on acrylates are the alkali soluble copolymers which contain carboxyl, methylol and esterified methylol derivatives of acrylamide. The production and properties of these copolymers have been the subject of a number of works [367, 407, 408]: copolymerization of acrylic acid with acrylamide and of the lower esters of acrylic acid in isopropyl alcohol with subsequent neutralization of the products with triethyl amine and methylolation with an aqueous solution of formaldehyde at 70°C have been described. It has been established [409] that the best properties are those of a copolymer containing acrylic acid (from 10 to 15%) and acrylamide (from 4 to 3 %). In these same works, hardening modes of the polymers produced were described and it was found that the optimal mode is heating of a specimen to 130°C for 30 minutes. Self-hardening film formers have also been produced, containing both carboxyl and epoxy groups [394]. These materials were produced by copolymerization of alkyl acrylates (75-90%) with methacrylic acid (7-20%) and glycidyl methacrylate (5-10%) in dioxane or directly in the aqueous phase, with subsequent neutralization by an aqueous ammonia solution.

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